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For: Polypropylene Homopolymers for Biaxially Oriented Films

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DECLARATION OF DR. SEHYUN KIM UNDER 37 C.F.R. § 1.132

I, Sehyun Kim, do declare that I am a citizen of the Republic of Korea, and that I reside at 4119 Windsor Court, Murrysville, Pennsylvania 15668. I received a Bachelor's of Engineering in Materials Science and Engineering from Korea University, Seoul, Korea in 1982. I attended the Master's program in Macromolecular Engineering at Case Western Reserve University in Cleveland, Ohio, and received a Master of Science Degree in Polymer Science from the University of Akron, Akron, Ohio in 1985. I received my Ph.D. in Polymer Science from the University of Akron, Akron, Ohio in 1990.

From 1989 to 1990 I was a Postdoctoral Research Associate at the A. E. Staley Manufacturing Company, Decatur, Illinois and the USDA, ARS-National Center for Agricultural Utilization Research, Peoria, Illinois. From 1990 to 1996 I was a Senior Staff Research Chemist for Fina Oil and Chemical Company, Deer Park, Texas. From 1996 to 1997 I was a Product Designer and Technologist for GE Plastics, Washington, West Virginia. Since 1998, I have been employed by Sunoco Chemicals (formerly

Aristech Chemicals), Pittsburgh, Pennsylvania, as a Polypropylene Materials Scientist and Intellectual Property Coordinator.

I have over 27 years of academic and industrial experience in the field of polymer science and I am well versed in the production of propylene homopolymers.

I am thoroughly familiar with the invention defined and claimed in U.S. Patent Application Serial Number 10/716,828.

The invention claimed in the present application, on which I am the named inventor, is related to the discovery that by controlling two known properties of polypropylene homopolymers in tandem, one can achieve surprisingly good and reproducible performance in the manufacture of biaxially oriented polypropylene (BOPP) films. The two properties that are controlled are the average meso-run length, as measured in the xylene insoluble fraction, and the quantity of the xylene solubles fraction as determined using method ASTM D5492-94. Both of these properties and methods for controlling them in polypropylene homopolymers are known in the art of polypropylene manufacture using Ziegler-Natta (ZN) catalysts. What was not previously known, and has now been discovered, is that by controlling these two properties in tandem to achieve certain values for each and a particular ratio of the two values, superior performance in the manufacture of BOPP films is achieved.

Because the properties of average meso-run length, as measured in the xylene insoluble fraction, and xylene solubles content, and methods for controlling these properties are known to those skilled in the art of polypropylene manufacture, one of ordinary skill in the art would be able to produce a polypropylene having the claimed properties. However, prior to the discovery that it is possible to achieve superior

performance in BOPP film production by achieving certain values for each property and a particular ratio of those values, one skilled in the art would not have been directed to produce a propylene homopolymer having those properties for BOPP film manufacture.

Average Meso-Run Length

It is known that the xylene insoluble fraction of a propylene homopolymer is made up of primarily isotactic, crystalline polypropylene, with some amount of amorphous (non-crystalline) material.

The meso-run length of the xylene insoluble fraction of a polypropylene homopolymer is a measure of the isotacticity and hence the crystallinity of the xylene insoluble fraction. The average meso-run length for the insoluble fraction of a given polymer is determined by ^{13}C NMR as disclosed in my patent application, and in the published PCT Application WO 96/04320 to Miro *et al.* This principle is discussed in WO 96/04320 in terms of a heptane insoluble fraction at page 3, lns. 10 to 14, and at page 7, ln 6 to page 9, ln. 5. However, the same principle is applicable when speaking of a xylene insoluble fraction. This principle is also discussed by Kissin *et al* in "Propylene Polymerization with Titanium-Based Ziegler-Natta Catalysts: Effects of Temperature and Modifiers on Molecular Weight, Molecular Weight Distribution and Stereospecificity", *Macromol. Chem. Phys.* 2004, *205*, 284-301. At page 285 of their paper, Kissin *et al* discuss the isotacticity of both heptane and xylene insolubles in terms of the "average" isotacticity of the insoluble fraction as measured by NMR. Published PCT Application WO 99/20663 to Randall *et al* discusses average meso-run length as a measure of the average level of isotactic polypropylene stereoregularities in polypropylene at page 7, lns. 19 to 25.

Xylene Soluble Fraction

The xylene soluble fraction, or alternatively the heptane soluble fraction, of a polypropylene homopolymer is typically used as a measure of amorphous (non-crystalline) material in a homopolymer, which is made up primarily of atactic polypropylene. Whether a xylene soluble or heptane soluble fraction is determined is based generally on the polymer being characterized, which is in turn a function of the catalyst system used. A discussion of the measurement of solubles content using the xylene method is discussed in detail in "Polypropylene and Other Polyolefins: Polymerization and Characterization", ©Elsevier Science Publishers B.V., 1990, Ser van der Ven, at pages 149 and 577-584. Generally, the higher the xylene soluble content in a polypropylene, the lower the crystallinity, melting point and flexural modulus of the material. As discussed in my patent application, some level of xylene solubles are desirable as they improve the processability of a polypropylene in the manufacture of BOPP films. Measurement of xylene soluble content in a polypropylene homopolymer is known and all of the above cited references discuss the measurement of xylene solubles, or heptane solubles.

Parameters Controlling Average Meso-Run Length and Xylene Soluble Content

As shown above, average meso-run length of the insoluble fraction and xylene solubles content are known and widely reported properties of propylene homopolymers.

Further, the general principles applicable to the control of both the average meso-run length as measured in the xylene insoluble fraction of a polypropylene homopolymer and the total content of xylene solubles in the homopolymer are known. In general, the average meso-run length in the xylene insoluble fraction is inversely related to the

quantity of xylene solubles, as disclosed in published PCT Application WO 96/04320 at page 2, lns. 21 to 27. Therefore, it is known that these two properties can be controlled together.

Several factors that will influence average meso-run length and xylene soluble content are: selection of the particular ZN catalyst itself (including internal electron donor), selection of a co-catalyst, selection of external electron donor(s), reaction temperature, and hydrogen concentration. All of these variables and methods to control them are known to those having skill in the art of polypropylene manufacture as is demonstrated by the disclosures of the academic and patent literature.

a)   Selection of the ZN Catalyst and Co-Catalyst

Of initial importance is the selection of a ZN catalyst. It is known that ZN catalysts are so-called multi-center catalysts. That is, the catalyst contains multiple active centers at which polymerization can occur. As disclosed by Kissin *et al* at pages 284-85, the multiple active centers in a single catalyst can be grouped into families which produce polymers of varying tacticity. In "Microtacticity Distribution of Polypropylenes Prepared with Heterogeneous Ziegler-Natta Catalysts", *Macromol.*, 1988, *21*, 314-319, Kakugo *et al* demonstrate in their Tables I and II the variation in isotacticity and xylene solubles content that can be obtained by using different ZN catalysts using the same co-catalyst. Kakugo *et al* also report that the isotactic (*mmmm*) pentad fraction decreases with increase in the xylene solubles content.

Ser van der Ven in "Polypropylene and Other Polyolefins: Polymerization and Characterization", ©Elsevier Science Publishers B.V., 1990, at page 59 discusses the necessity of an internal electron donor modified catalyst for the production of highly

isotactic polypropylene using supported catalysts. In "Effect of Internal Donors in Propylene Polymerization Analyzed with Two-Site Model", *Polym. Int.*, 51, 530-533, 2002, Shimozawa *et al* demonstrate the effect of the content of internal donor on the tacticity of polypropylene produced using supported ZN catalysts.

The effect of co-catalysts on materials produced using ZN catalysts is also discussed in detail by van der Ven at pages 50-70. Also discussed is the effect of the ratio of internal donor to co-catalyst on stereoselectivity.

Further, published PCT Application WO 96/04320 discloses throughout that critical amounts of diethylaluminum chloride as a co-catalyst and certain silane electron donors can be used in conjunction with ZN catalysts to provide polypropylenes having a desirable meso-run length in a heptane insoluble fraction without a significant increase in atatic (soluble) content. See for example page 9, lns. 23 to 33.

b)   External Donors

In general, external electron donors are used as stereoregulators for supported ZN catalysts, as well as to regulate the activity of the catalysts. Kissin *et al* discuss the use of external donors, such as alkyl silanes, to regulate the activity and stereoselectivity of supported ZN catalysts, by selective poisoning of active centers that produce atactic polymer. Kissin *et al* report specifically at page 295 the marked increase in isotacticity in the xylene insoluble crystalline fraction of a polypropylene produced with a silane modifier.

Published PCT Application WO 99/20663 discloses that various external electron donors will modify the stereospecificity of a given ZN catalyst to different extents. Published PCT Application WO 99/20663 further discloses that external donors may be

used in combination to achieve desired properties in a polypropylene. For example, the disclosure compares tetraethoxysilane (TEOS) and dicyclopentyldimethoxysilane (DCPMS), with DCPMS being a more stereoregulating external donor.

U.S. Patent 6,635,734 to Shamshoum *et al* disclose that it is known that certain ZN catalysts may work particularly well with a certain compound or class of compounds as electron donor(s). U.S. Patent 6,635,734 discloses particular combinations of ZN catalysts and electron donors that yield high crystallinity and good control of xylene solubles.

As stated above, published PCT Application WO 96/04320 discloses that critical amounts of diethylaluminum chloride and certain silane electron donors can be used in conjunction with ZN catalysts to provide polypropylenes having a desirable meso-run length in a heptane insoluble fraction without a significant increase in atatic content.

c)   Temperature Effects

Kissin *et al* discuss the effects of temperature on the stereospecificity of a given catalyst. As reported by Kissin, increases in reaction temperature result in a decrease in the average molecular weight of the polymer produced by a catalyst system. The increase in temperature also results in a decrease in the crystalline fraction and a corresponding increase in the xylene soluble fraction. In addition, Kissin *et al* report that the content of highly isotactic material in the crystalline fraction increases with temperature.

d)   Effect of Hydrogen

Hydrogen is used in the polymerization of propylene to affect the molecular weight of the product polypropylene. In published PCT Application WO 99/20663,

Randall *et al* demonstrate the impact of varying the hydrogen concentration on the melt flow rate and molecular weight of polypropylene produced with various external electron donors. In particular, the disclosure of Randall *et al* shows that the effect of hydrogen on molecular weight is related to the hydrogen response of the external donor used.

What has been Discovered According to the Current Invention

What was not previously known by those skilled in the art, and what has been discovered, is that by using the above known techniques to control the average meso-run length as measured in the xylene insoluble fraction of a propylene homopolymer, and the xylene soluble content of the polymer within specified parameters, surprisingly good and reproducible processability in BOPP film production can be obtained.
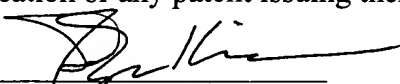
Specifically, as disclosed and claimed in my patent application, it has been discovered that if the meso-run length N_m of the xylene insoluble fraction is controlled so that it is equal to or less than 130, while at the same time the xylene solubles are controlled so that the ratio of the meso-run length of the insoluble fraction to the total xylene solubles, as determined using method ASTM D5492-94, is less than 22, the resulting polypropylene homopolymer displays surprisingly good performance in the production of BOPP films. Table 1 in my patent application shows various combinations of average meso-run length and xylene solubles contents that are within the scope of the invention, particularly examples D through J.

Once this discovery is known, one of ordinary skill in the art will be able to select a combination of catalyst, co-catalyst and external donor, along with appropriate reaction conditions, such as temperature and hydrogen pressure, to obtain polymers having these properties. Although some experimentation may be necessary to fine tune a

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polymerization process to obtain the correct properties in the polymer produced, it would only involve adjustment of parameters already known to effect those properties of the polymer. Such routine experimentation is always necessary when implementing a new product or process in a commercial scale polymerization reactor train.

The invention claimed in the current application is not a method for controlling the average meso-run length of the xylene insoluble fraction, and xylene solubles content in a polypropylene. As discussed above, and shown by a review of the open literature, the methods for controlling these two properties in the polymerization of propylene are known by those skilled in the art. The invention is the discovery that by using these known techniques to control the average meso-run length as measured in the xylene insoluble fraction so that it is 130 or less, and the content of xylene solubles in the polymer within the disclosed and claimed ranges so that the ratio of the average meso-run length to xylene solubles is less than 22, surprisingly good and reproducible results in BOPP film manufacture are obtained. Therefore, I believe that one having ordinary skill in the art would be able to practice the novel features of my invention.

I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

_____   ___11/18/2005___
Dr. Sehyun Kim   Date

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(54) Title: HIGH IMPACT, FLEXURAL MODULI POLYMERIC MATERIALS FORMED USING SEQUENTIAL DONORS

HYDROGEN RESPONSE FOR DCPMS AND TEOS

(57) Abstract

A method of forming high impact copolymer having a high degree of crystallinity and a melt flow rate of at least 10 to 150. The method preferably comprising: subjecting the α-olefin monomer to an initial polymerization, in the presence of a first electron donor material and a first catalyst to form a polymer product; subjecting the polymer product to a subsequent polymerization, in the presence of a second electron donor material and a second catalyst, thereby forming the α-olefin homopolymer; wherein the second donor material is more stereoregulating than the first electron donor material and the second electron donor material dominates the first electron donor material; and polymerizing a copolymer in the presence of the α-olefin homopolymer; thereby forming a high impact copolymer. The first and second catalysts may be the same or different. The copolymer portion of the high impact copolymer will have an unexpected high amorphous phase content.

APPLICATION FOR U.S. PATENT

HIGH IMPACT, FLEXURAL MODULI POLYMERIC MATERIALS
FORMED USING SEQUENTIAL DONORS

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FIELD OF THE INVENTION

This invention relates to novel high impact, high flexural moduli polymeric materials, i.e., in situ polymerized polypropylene homopolymers and polypropylene copolymers, formed by a sequential polymerization process in which a different

10   electron donor material is used during the initial and subsequent polymerization steps. In particular, the present inventors have discovered that the second donor material must be more stereoregulating than the first electron donor material and the second electron donor material must also dominate the first electron donor material in order to form in situ polymerized homopolymers and copolymers which

15   exhibit unusually good balances of impact resistances and flexural strengths.

BACKGROUND OF THE INVENTION

The physical properties of homopolymers and copolymers of propylene formed by typical Ziegler-Natta polymerization are highly dependent on the

20   stereoregularity of the polymer itself. Highly stereoregular polymers are crystalline, provide a desirable high flexural moduli and are formed with a suitable choice of electron donor. These highly crystalline polymers also display high melting points, but innately exhibit low melt flow rates (MFR) that render them unsuitable for applications that require high processing rates, such as in injection

25   moldings, oriented films and thermobound fibers. Further, conventional polypropylene homopolymer and copolymer products formed from highly crystalline polypropylenes lack sufficient impact resistance.

The addition of various electron donor materials to Ziegler-Natta catalysts has been known to influence the degree of stereoregularity in polypropylene

30   homopolymers and copolymers. Generally, a single base catalyst (e.g., a magnesium chloride supported base Ziegler-Natta catalyst) can be used in

combination with any number of electron donor materials, each of which, or combination of which, will lead to a specific level of stereoregularity and MFR. One of the properties of electron donors is that the polypropylene MFR, at the same reactor hydrogen level, decreases with increasing polypropylene

5   stereoregularity caused by the donor. Additional hydrogen is required to reach desirable MFRs when highly stereoregulating donors are employed. This relationship between stereoregularity and MFR poses a problem in processes that have hydrogen pressure limitations. In those processes where the desirable hydrogen pressure cannot be reached, a more hydrogen responsive donor material

10   must be used. Such donor materials, however, lead to the formation of less stereoregular polypropylenes with more amorphous polypropylene by-products that produce polypropylenes which lack sufficient flexural moduli. Thus, processes that have hydrogen pressure limitations pose a problem because the final achievable MFR will be determined by the choice of electron donor, which in turn determines

15   the level of polypropylene stereoregularity in the final product.

Therefore, it would be highly desirable to synthesize homopolymers and copolymers in an in situ polymerization process to make high impact copolymers (ICP) that have both high flexural moduli and high MFRs. The present inventors have discovered that the sequential additions of electron donor materials in

20   polymerization reactors connected in series is required to achieve polymers at higher MFRs and at higher levels of crystallinity, where one type of donor is placed in the first reactor and a second type of donor is placed in the second (or subsequent) reactor. It has been found by the present inventors that the sequential use of the two donors broadens both the molecular weight distribution and the

25   compositional distribution of the homopolymer components and provides a more crystalline homopolymer having product characteristics closer to the same polymer formed in the presence of the more stereoregulating donor material by itself. That is, the crystallinity and flexural moduli of the resulting in situ polymerized ICP are higher than expected from the weighted average of the two independent donor

30   products, but the final MFR can be predicted from the weighted average of the independently produced donor products.

The present inventors have also discovered that the choice of electron donor materials affects the downstream ethylene-propylene (E/P) copolymer components produced in an impact copolymer (ICP) process where one or more gas phase reactors are placed downstream from the series of polypropylene homopolymer reactors. That is, the present inventors have unexpectedly discovered that if a combination of donors are selected where the higher stereoregular donor dominates over the lesser stereoregular donor, then the nature of copolymer produced downstream from the homopolymer reaction stage is desirably affected only by the higher stereoregulating donor.

SUMMARY OF THE INVENTION

Novel high impact copolymer in situ polymerized materials (e.g., polypropylene in combination with poly(ethylene-co-propylene)) with substantial degrees of crystallinity and high MFRs can be produced by sequentially adding first and second electron donor materials to a first and second (or subsequent) of a series of reactors, respectively; provided that the second electron donor material is more stereoregulating than the first electron donor material and provided that the second electron donor material dominates the first electron donor material.

A method is presented for forming in situ polymerized homopolymer components that have a broad molecular weight distribution and displays a high flexural moduli indicative of a highly crystalline, isotactic polymer, concurrently with a high MFR. Previously, high MFRs were exhibited only by lesser stereoregular polymers having a higher amorphous content. The method includes the subjection of an α-olefin (e.g., propylene, 1-butene, 1-pentene, 1-hexene, etc.) to an initial polymerization in a first reactor, in the presence of a first electron donor material and a supported Ziegler-Natta catalyst, thereby forming a polymer reaction product and subsequently continuing the polymerization of the polymer reaction product in a second reactor, in the presence of a second and different electron donor material with the same Ziegler-Natta catalyst provided that the second donor material is more stereoregulating than the first electron donor material and provided that the second electron donor material dominates the first

electron donor material. The unique homopolymers formed in accordance with the sequential donor process set forth immediately above are subjected to a further polymerization stage with the same catalyst system where in situ polymerized poly(ethylene-co-propylene)s are formed, thereby creating a high impact

5   copolymer (ICP) that exhibits a superior balance of flexural moduli and impact resistance with the appropriate choice of sequential electron donor materials.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph plotting MFR versus hydrogen pressure for

10   tetraethoxysilane (TEOS) and dicyclopentyl dimethoxysilane (DCPMS) electron donors;

Fig. 2 is a graph plotting MFR versus the level of DCMPS in polymerizations using mixed (1) TEOS/DCPMS and mixed (2) PTES/DCPMS

15   donors at a constant hydrogen level of 150 psig;

Fig. 3 is a graph plotting heats of fusion versus the level of DCMPS in polymerizations using mixed TEOS/DCPMS donors at a constant hydrogen level of 150 psig;

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Fig. 4 is a schematic depicting stereoregularity (meso run length (MRL)) and its distribution with sequential and single donors;

Fig. 5 is a graph plotting weight % xylene solubles versus 1% Secant

25   Flexural Modulus for both single and sequential donors;

Fig. 6 is a graph plotting weight % xylene solubles versus 1% Secant Flexural Modulus comparing the effect of nucleation on a polymer formed with a single electron donor and a polymer formed with sequential donors;

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Figs. 7a and 7b are bar graphs comparing the Gardner Impact strengths of a pigmented polymer formed with a single electron donor and a pigmented polymer formed with sequential donors at both room temperature (i.e., 25°C) and at -29°C, respectively; and

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Fig. 8 is a graph plotting the total copolymer weight % ethylene versus the weight % amorphous ethylene/propylene copolymer in high impact polypropylene copolymers polymerized in the presence of a single electron donor and sequential electron donors.

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DETAILED DESCRIPTION OF THE INVENTION

The homopolymer components of the in situ polymerization of polypropylene and poly(ethylene-co-propylene) of the present invention possess a broad molecular weight distribution and simultaneously display high flexural moduli, normally associated with highly crystalline polymers, and a high melt flow rate (MFR), normally associated with less stereoregular polymers. These novel homopolymer components are formed in a process where, for example, propylene is sequentially subjected to an initial polymerization in the first series of reactors and in the presence of a Ziegler-Natta catalyst and a first electron donor material. This polymerization is continued in a second reactor where a subsequent or second polymerization reaction occurs in the presence of the same Ziegler-Natta catalyst but with a second electron donor material. The second electron donor material should be more stereoregulating than the first electron donor material. The second electron donor material should also dominate the first electron donor material.

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The Ziegler-Natta catalyst useful in the practice of the present invention is a solid titanium supported catalyst system described in US-A-4990479 and US-A-5159021. Briefly, the Ziegler-Natta catalyst can be obtained by: (1) suspending a dialkoxy magnesium compound in an aromatic hydrocarbon that is liquid at ambient temperatures; (2) contacting the dialkoxy magnesium-hydrocarbon composition with a titanium halide and with a diester of an aromatic dicarboxylic

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acid; and (3) contacting the resulting functionalized dialkoxy magnesium–hydrocarbon composition of step (2) with additional titanium halide.

The Ziegler-Natta co-catalyst is preferably an organoaluminum compound that is halogen free. Suitable halogen free organoaluminum compounds are, in particular, branched unsubstituted alkylaluminum compounds of the formula AlR_3, where R denotes an alkyl radical having 1 to 10 carbon atoms, such as for example, trimethylaluminum, triethylaluminum, triisobutylaluminum and tridiisobutylaluminum. Additional compounds that are suitable for use as a co-catalyst are readily available and amply disclosed in the prior art including US-A-4,990,477, which is incorporated herein by reference. The same or different Ziegler-Natta catalyst(s) can be used in both the initial and subsequent polymerization steps.

Electron donors are typically used in two ways in the formation of Ziegler-Natta catalysts and catalyst systems. An internal electron donor may be used in the formation reaction of the catalyst as the transition metal halide is reacted with the metal hydride or metal alkyl. Examples of internal electron donors include amines, amides, ethers, esters, aromatic esters, ketones, nitriles, phosphines, stilbenes, arsines, phosphoramides, thioethers, thioesters, aldehydes, alcoholates, and salts of organic acids. In conjunction with an internal donor, an external electron donor is also used in combination with a catalyst. External electron donors affect the level of stereoregularity and MFR in polymerization reactions. External electron donor materials include organic silicon compounds, e.g. tetraethoxysilane (TEOS) and dicyclopentydimethoxysilane (DCPMS). Internal and external-type electron donors are described, for example, in US-A-4,535,068, which is incorporated herein by reference. The use of organic silicon compounds as external electron donors are described, for example, in U.S. Patent Nos. 4,218,339, 4,395,360, 4,328,122 and 4,473,660, all of which are incorporated herein by reference. The preferred electron donors of the present invention are external electron donors used as stereoregulators, in combination with Ziegler-Natta catalysts. Therefore, the term "electron donor", as used herein refers specifically to external electron donor materials.

The external electron donor acts to control stereoregularity, which affects the amount of isotactic versus atactic polymers. The more stereoregular isotactic polymer is more crystalline, which leads to a material with a higher flexural modulus. Highly crystalline, isotactic polymers also display lower MFRs, as a consequence of a reduced hydrogen response during polymerization. The stereoregulating capability and hydrogen response of a given electron donor are directly and inversely related. The DCPMS donor has a substantially lower hydrogen response than the TEOS donor, but produces a significantly higher level of stereoregularity than TEOS. Because DCPMS is more stereoregulating, it will, at an equal reactor hydrogen pressure, provide a higher level of crystallinity and lower MFR than the lesser stereoregulating TEOS donor.

In the following examples, two different catalyst formulations, which are used to prepare ICPs with similar compositions, are compared. The first is catalyst A, a magnesium chloride supported, titanium-based Ziegler-Natta catalyst system, with sequential donors in serially connected reactors; TEOS (donor A) is used in the first reactor and DCPMS (donor C) in the second reactor. The second catalyst B, is also a magnesium chloride supported, titanium-based Ziegler-Natta catalyst system, with the single cyclohexylmethyldimethoxysilane (CMMS) electron donor B in both reactors. The average level of isotactic polypropylene stereoregularities for these two catalysts are similar as measured by the average *meso* run lengths (MRL) of the in situ produced polypropylene homopolymers. The MRL is determined from the [*mmmr*] fraction from ^{13}C NMR data and is given in Table 1 for these two catalyst formulations.

$$MRL = 2/[mmmr]$$

(See *Macromolecules* 1997, 30, 803, which is incorporated herein by reference.)

Table 1

(ISOTACTIC POLYPROPYLENE COMPONENT
STEREOREGULARITIES OF SINGLE (Catalyst B/CMMS) AND
SEQUENTIAL DONORS (Catalyst A/TEOS/DCPMS) PRODUCED ICPS)

ICP	AVERAGE MESO RUN LENGTHS	
#	SINGLE DONOR	SEQUENTIAL DONOR
1	223	224
2	200	199
3	180	196
4	235	209
5	240	
6	207	
7	223	
8	179	
9	191	
10	197	
11	197	
12	217	

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The donors, TEOS, CMMS and DCPMS produce different levels of
stereoregularities when used independently with either of the above catalysts to
produce isotactic polypropylene. With Catalyst A, the following stereoregularities
have been observed independently with the TEOS, CMMS and DCPMS donors.

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Table 2

(Average *Meso* Run Lengths Observed for Different Single Donors with
Catalyst A)

	TEOS	CMMS	DCPMS
MRL	150-180	200	400

15   A range of MRL values is given for the TEOS donor because the level of
stereoregularity of the TEOS donor will also rise with increasing levels of
hydrogen; whereas the CMMS and DCPMS donors produce stereoregularities that
are less dependent on hydrogen concentration.

Both the compositional and molecular weight distributions of the polypropylene homopolymer components will be broader with the sequential donors over that obtained with the single donor. The average MRLs are both lower and higher for the individual sequential donors, TEOS and DCPMS,

5   respectively, over that for the CMMS donor, as seen in Table 2. Consequently, the breadth of polypropylene stereoregularity will be wider for the sequential donors, even when the *average* stereoregularity is the same for sequential versus single donor polymers, as shown in Table 1. A similar argument holds true for the molecular weight distribution. The MFRs are both lower and higher for the

10   individual TEOS and DCPMS donors, respectively, over the CMMS donor at the same hydrogen level. A 35/65 blend of a 22 MFR homopolymer and a 160 MFR homopolymer, having a blended MFR of 80, will have a broader MWD than an 80 MFR homopolymer made with a single donor and the same catalyst system.

15   EXAMPLE 1

At 150 psig (1.13 MPa) hydrogen and in the presence of Catalyst A, the use of TEOS as an electron donor led to an MFR of 214 dg/min., a melting point (M.P.) of 157.9°C and a heat of fusion of 108.7 J/g. To the contrary, the same molar concentration of DCPMS electron donor resulted in a MFR of only 4.1, a

20   M.P. of 163.5°C and a heat of fusion of 110.2 J/g in the presence of Catalyst A and a hydrogen pressure of 150 psig (1.13 MPa). Fig. 1 plots MFR versus hydrogen pressure for TEOS and DCPMS electron donors. The data is given in Table 3 below.

<u>Table 3</u>

(HYDROGEN PRESSURE VERSUS MFR FOR ELECTRON DONORS,

TEOS AND DCPMS)

H$_2$	DCPMS	TEOS
psig	MFR(dg/min)	MFR(dg/min)
10		3.1
20		7.4
40		31.2
40		
80	1.8	53.2
80	1.7	89.2
80	1.3	
80	1.9	
80	1.5	
80	0.93	
80	1.5	
150	4.1	197
150		229
170	7.8	
200		321
300	12.5	
350	12.5	

5   Additionally, the hydrogen response of a donor controls molecular weight

of the polymer produced. The TEOS electron donor material exhibited a high

hydrogen response leading to a low molecular weight polymer product, while the

DCPMS electron donor material exhibited a low hydrogen response leading to a

high molecular weight polymer product.

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<u>EXAMPLE 2</u>

The tendency of one donor to dominate can be determined by examining

the MFR and final crystallinity of the polyolefin produced with a mixture of the

two donors at different relative concentrations. In plots of MFR (Fig. 2) and heats

15   of fusion, i.e., as a measure of crystallinity, (Fig. 3) versus the level of DCPMS in

polymerizations of propylene using mixed TEOS/DCPMS at a constant hydrogen

pressure of 150 psig (1.13 MPa), the dominance of DCPMS over TEOS is clearly

established. When the TEOS/DCPMS mixture contains only 10% DCPMS, both

the resulting MFR and heat of fusion are the same or better than those achieved
with DCPMS alone. A complete set of data corresponding to Figs. 2 and 3 are
provided in Tables 4 and 5, respectively. Also included in Fig. 2 is an example of
two mixed donors that show an example where neither donor has a dominating

5   effect. Propyltriethoxy silane (PTES) and DCPMS were used. In this case the
MFR closely follows what one might expect of such a mixture, an MFR close to
the average of the two donors.

Table 4

10   (DOMINANCE OF DCPMS OVER TEOS AND NON-DOMINANCE OF
DCPMS OVER PTES: MFR VERSUS % DCPMS IN A MIXTURE OF
TEOS/DCPMS AND PTES/DCPMS AT A CONSTANT HYDROGEN
PRESSURE OF 150 PSIG)

	TEOS/DCPMS	PTES/DCPMS
% DCPMS (remainder TEOS)	MFR	MFR
0	197	59
0	229	
5	10	
10	4.4	40
16	2.4	
25	4.5	27
30	8.7	
50	4.4	11
50	2.1	
50	6.4	
50	4.5	
75	2.6	
100	4.1	4.1

Table 5

(DOMINANCE OF DCPMS OVER TEOS: HEATS OF FUSION VERSUS % DCPMS IN A MIXTURE OF TEOS/DCPMS AT A CONSTANT HYDROGEN PRESSURE OF 150 PSIG)

% DCPMS	ΔH (J/g)	MFR
0	107	229
5	108	10
10	113	4
30	114	9
50	113	6
75	115	3
100	110	4

5

EXAMPLE 3

In accordance with a preferred embodiment according to the present

invention a propylene homopolymer may be formed using a sequence of

polymerization reactions. In the initial polymerization reaction, 625 grams of

10   propylene are polymerized to form 320 grams of polypropylene in the presence of

0.008 grams of Catalyst A and 0.0416 grams of a relatively weak stereoregulating

electron donor (TEOS). The resulting propylene homopolymer has a moderate

stereoregularity as measured by ΔH_f and an MFR of 160. The reaction mixture of

the initial polymerization reaction is then passed to a second reactor where further

15   polymerization is conducted in the presence of 0.0456 grams of a more

stereoregulating, dominant electron donor (DCPMS). The TEOS from the first

polymerization passes to the second stage so that the further polymerization is

conducted in the presence of a mixture of TEOS and DCPMS in a weight ratio of

one to one. However, since the DCPMS dominates the TEOS, 50% of the

20   polymer created in the second reactor closely resembles a polymer formed in the

presence of DCPMS alone. The second reactor polymerization produces a higher

isotactic (MRL of approximately 400), lower MFR (22) polymer which leads to a

blended MFR of 80 and an average MRL of 200. Each of the first and second

reactors can be, for example, a bulk liquid slurry stirred tank reactor.

Using the same hydrogen content in each of the reactors, the final, average MFR of a polypropylene homopolymer exiting the second reactor is nominally one half the MFR of the product leaving the first reactor. The deblended MFR (i.e., a calculated MFR of the component product from the second reactor) of a polypropylene produced in the second reactor is substantially lower than the average MFR of the homopolymer residing in the first reactor. As shown in Table 6, the MFR in the first reactor is 160 using TEOS as the electron donor material and the blended MFR in the second reactor is 80 using DCPMS as the electron donor material. The deblended MFR in the second reactor is calculated to be 22, using the equation below and wherein $w_1 = 0.649$ and $w_2 = 0.351$ are the production splits in weight fractions in reactors 1 and 2, respectively.

$$\log(MFR_{reactor\ 2}) = (\log(\text{blended } MFR_{reactor\ 2}) - w_1\log(MFR_{reactor\ 1}))/\ w_2$$

TABLE 6

MFR IN FIRST REACTOR (TEOS)	AVERAGE MFR IN SECOND REACTOR (DCPMS)	DEBLENDED* MFR IN SECOND REACTOR (DCPMS)
160	80	22
140	70	14
80	27	2.4
60	23	4.9

* Calculated MFR in the second reactor.

Once again, the sequential addition of donors leads to a broadening of both the molecular weight distribution and the chiral or stereoregularity distribution of the resulting polypropylene homopolymers. If the stereoregulating capabilities of the donors that produce the high MFR (donor A, e.g., TEOS) and low MFR (donor C, e.g., DCPMS) homopolymers have the following relationship to the single donor that produced independently the median MFR (donor B, e.g., CMMS) homopolymer,

Donor C > Donor B > Donor A

(More Stereoregular → Less Stereoregular)

then the chiral or stereoregularity distribution of the in situ blend will be broader

for the sequential donors C and A. Such a broadening of the chiral distribution is

illustrated in Fig. 4. Correspondingly, the donor hydrogen responses, at the same

5   hydrogen concentration, that obey the following MFR relationships

Donor C < Donor B < Donor A

(Lesser H_2 Response → Greater H_2 Response)

10   will lead to a broader MWD for the sequential donors than the single donor.

The stereoregularity of the propylene homopolymer formed as set forth

above ranges from moderate, an average of 150-180 MRL, for the TEOS

produced polypropylenes to an average of approximately 400 MRL for the

DCPMS produced polypropylenes. Each of these polypropylene components has a

15   distribution surrounding its average stereoregularity. Each of these distributions

also incrementally increase in stereoregularity with incremental increases in

molecular weight. It has been demonstrated through fractionation studies that the

stereoregularities of isotactic polypropylenes, produced with a supported Ziegler-

Natta catalyst in conjunction with an electron donor, increase with increasing

20   molecular weight. (See *Polymer* 1994, 25, 2636, which is incorporated herein by

reference). The approximately 400 MRL component will have molecules in the

upper end of the stereoregular distribution that have MRLs of over 1000. The

presence of this high molecular weight, highly stereoregular component leads to a

higher flexural modulus than observed for polypropylenes with the same average

25   stereoregularity but with a more narrow distribution. The primary reason for this

higher flexural modulus is that the high molecular weight, highly isotactic

components crystallize first, and then serve as a template for the lesser

stereoregular polypropylenes during crystallization.

The polypropylene crystallinities prepared with the CMMS donor and with

30   the sequential TEOS/DCPMS donor system are therefore significantly different, in

spite of similar average polypropylene stereoregularities and similar E/P copolymer

contents. It is well known to those skilled in the art that observed flexural moduli are a direct function of the level of crystallinity. Evidence for the differences in breadths of the stereoregularity distributions causing different crystallinities is apparent from the higher 1% secant flexural moduli provided by the ICPs produced

5   with the sequential TEOS/DCPMS donors, as shown in Fig. 5 and given in Table 7. The flexural moduli data are presented as a function of xylene solubles content; this xylene soluble fraction contains both the amorphous component of the poly(ethylene-co-propylene) copolymer and atactic polypropylene component of the homopolymers and copolymers. Both of these components soften the

10   polypropylene matrix, thereby reducing the flexural modulus. The E/P copolymer, however, contributes to much improved impact strengths, which is the purpose for preparing the in situ blend.

TABLE 7

1% SECANT FLEXURAL MODULI OF UN-NUCLEATED ICPS AT GENERALLY THE SAME MESO RUN LENGTH PREPARED BY SINGLE AND SEQUENTIAL DONORS AS A FUNCTION OF XYLENE SOLUBLES CONTENT (a-PP + a-E/P)

ICP #	SEQUENTIAL DONORS		SINGLE DONOR	
	% Xylene Solubles	1% Secant Flexural Modulus	% Xylene Solubles	1% Secant Flexural Modulus
1	7.16	219		
2	8.14	187		
3	8.35	206		
4	8.39	215	8.41	188
5	8.56	219		
6	8.79	190		
7	8.87	190		
8	9.24	216	9.06	177
9	9.46	205		
10	9.59	198		
11	9.80	211	10.00	187
12	10.48	172		
13	11.09	186	11.06	172
14	11.50	208		
15	11.99	194	11.92	150
			11.92	170
16	12.25	190		
17	13.95	192	13.65	168
18	14.24	198		
19	14.45	188	14.63	164
			15.35	173
			15.82	143
20	16.65	184	16.23	159
			16.56	165
21	16.91	177		
22	17.36	181		
23	17.46	168		
24	19.89	172		
25	22.66	144		
26	24.02	139		
27	26.65	118		
28	27.10	118		

The 1% secant flexural moduli of ICPs prepared with sequential TEOS/DCPMS donors and Catalyst A obey the following relationship:

1% Secant Flexural Modulus = -4.43(wt.% xylene solubles) + 254.5 (Eq. A)

wherein wt.% xylene solubles is the weight percent of the ICP that remains solublized in xylene at room temperature (21-25°C), and signifies the wt.% of the ICP that is totally amorphous and cannot crystallize at room temperature. The amorphous components of an ICP (atactic polypropylene and amorphous ethylene/propylene copolymers) have a negative influence on the flexural modulus, which again is predominantly a function of crystallinity.

The single CMMS donor-produced ICPs, in contrast, exhibited a 1% secant modulus in accordance with the following relationship:

1% Secant Flexural Modulus = -3.00(wt.% xylene solubles) + 209.5 (Eq. B)

These equations were developed for polymers with average meso run length of 200 and are operative for a range of 170-250 average meso run length, as shown in Table 1.

The 1% Secant Flexural Modulus of sequential donor produced ICPs will be at least 5%, preferably 10%, more preferably 15%, most preferably 20% greater than that described by Equation B for a given xylene solubles level (See Fig. 5). These observed differences in 1% secant flexural moduli, given above, are caused by the fact that highly stereoregular, high molecular weight homopolymers influence the crystallization process of polypropylene. The DCPMS component of the sequential TEOS/DCPMS donors leads to polypropylene components with very high stereoregularities that are not produced to the same extent with the CMMS donor, such that the final crystallinity is closer to that produced by the more stereoregulating donor, DCPMS. This allows a higher crystallinity (and resulting higher flexural moduli) than can be provided by a polypropylene having the same overall average stereoregularity that is formed using a single donor with a

lesser breadth of the stereoregularity distribution. At the same time, the observed MFR is a logarithmic average of that produced by the sequential donors, TEOS, which leads to a high MFR and DCPMS, which leads to a low MFR.

5

EXAMPLE 4

A high impact copolymer (ICP) according to the present invention can be formed by polymerizing *in situ*, that is, in the presence of the propylene homopolymer of Example 3 and with the same catalyst system, a copolymer formed from 20 to 80% ethylene and 80 to 20% of propylene in a third (and

10   fourth) reactor, typically a gas phase reactor(s). The composition of the final product is an ICP having between 1 to 50% of an ethylene/propylene copolymer, and 99 to 50% of a propylene homopolymer. The total percent ethylene content of the ICP formed above ranges from 1 to 25% and the ICP has an MFR from 10 to over 100. Conventional ICPs have a MFR of from 0.3 to 100.

15

Polymerization Process for the Synthesis of Impact Copolymer

The continuous polymerization process referred to above as in situ polymerization consists of two bulk liquid reactors in series followed by one or more gas phase reactors. Generally, homopolypropylene is polymerized within the

20   bulk liquid reactors followed by ethylene-propylene copolymerization in one or more gas phase reactors. The final product is typically called an "ICP". The donor system in the process could be a single donor such as cyclohexylmethyldimethoxysilane (CMMS) or sequential donors such as tetraethoxy silane (TEOS) and dicyclopentyldimethoxy silane (DCPMS). The

25   concentration of the donor is similar in the two liquid bulk reactors in the case of single donor and different in the case of sequential donors, resulting in either the same MFR polypropylene in the two reactors with a single donor type and completely different MFRs with sequential donors. The resultant polymer is transferred to the gas phase reactor wherein an ethylene-propylene copolymer is

30   polymerized.

Typical Polymerization Conditions for a Single Donor with Catalyst B

The temperatures within the bulk liquid reactors and gas phase reactor is 158°F (70°C). The hydrogen and triethylaluminum (TEAL) concentrations in the first bulk liquid reactor are 3595 ppm and 75 ppm respectively. The CMMS

5   concentration in the liquid bulk reactors is 25 ppm. The hydrogen concentration in the second liquid bulk reactor is 1950 ppm, resulting in a polypropylene MFR of 53 to 55 dg/min. The production splits in the two liquid bulk reactors were 65:35 (first:second). The hydrogen concentration in the gas phase reactor is 55,000 ppm, and ethylene monomer to the ethylene plus propylene monomer ratio is 0.45 and

10   the reactor pressure is 190 psig (1.41 MPa). The ethylene content in the ethylene-propylene copolymer is 57.5 wt.%, and a total rubber level of 14 to 15 wt.%. The final MFR of ICP is 33-37 dg/min.

Typical Polymerization Conditions for Sequential Donors with Catalyst A

15   The continuous polymerization process is similar to the single donor example, but with some changes in the donor systems in the liquid bulk reactors. The donor systems in this process are called sequential donors, because two different donors are used, namely tetraethoxy silane (TEOS) in the first liquid bulk reactor and TEOS and dicyclopentyldimethoxy silane (DCPMS) in the second bulk

20   liquid reactor. In the first bulk liquid reactor, the donor TEOS produces a high MFR polypropylene, and in the second bulk liquid reactor the combination of TEOS and DCPMS produces a low MFR polypropylene which is attributed to the dominance of DCPMS donor in presence of TEOS.

The hydrogen and triethylaluminum (TEAL) concentrations in the first bulk

25   liquid reactor are 1670 and 57 ppm, respectively. In the second liquid bulk reactor the hydrogen and TEAL concentrations are 1550 and 57 ppm, respectively. The TEOS concentration in the first liquid bulk reactor is 21.4 ppm, resulting in a polypropylene MFR of between 130-140 dg/min, and the concentrations of TEOS and DCPMS in the second liquid bulk reactor are 21.5 and 36.6 ppm, resulting in a

30   de-blended MFR of between 20-22 dg/min or a blended MFR of the two reactors of 69-75 dg/min. The production splits in the two liquid bulk reactors were 65:35

(first:second). The hydrogen concentration in the gas phase reactor is 38,000 ppm, and ethylene monomer to the ethylene plus propylene monomer ratio is 0.35 and the reactor pressure is 190 psig (1.41 MPa). The ethylene in the ethylene-propylene copolymer is 50-55 wt.%, and a total copolymer level of between 15 to

5   15.4 wt.%. The final MFR of ICP is between 35-38 dg/min.

ICPs formed with the propylene homopolymers of the present invention are superior to ICPs formed with single donor-formed polypropylene for a number of reasons. Ethylene/propylene copolymers produced downstream from sequential donor-prepared polypropylene have both crystalline and amorphous components.

10   (Such polymers are referred to as "bipolymers" and are characteristically produced by Ziegler-Natta catalysts typically used in the highly stereoregular polymerizations of α-olefins). It is the amorphous component of the ethylene/propylene copolymer that is the "rubber-like" copolymer. It was discovered by the present inventors that the ratio of amorphous to crystalline portions of the copolymer is related to the

15   stereoregulating ability of the catalyst system, which is influenced by the choice of electron donor material. The resulting level of crystallinity of a particular copolymer will vary, based upon the electron donor material that is used in the upstream homopolymer polymerization steps. The level of copolymer crystallinity caused by a particular electron donor material is as follows:

20

TEOS $\geq$ CMMS > DCPMS.

(More Copolymer Crystallinity $\rightarrow$ Less Copolymer Crystallinity)

Because amorphous ethylene/propylene copolymers are required to provide

25   high impact resistance in an ICP, it is highly desirable that these ICPs comprise a high percentage of amorphous copolymer within the bipolymer. DCPMS provides the lowest level of crystalline ethylene/propylene copolymers. However, because of its low hydrogen response, DCPMS can only be used to produce low MFR ICPs. The TEOS/DCPMS sequential donor catalyst system according to the

30   present invention has an excellent overall hydrogen response, which leads to ICPs having MFRs in the range of between 5 to 100. Further, because DCPMS

dominates TEOS, the TEOS/DCPMS sequential donor catalyst system produces bipolymers as if DCPMS were the only donor. Therefore, the TEOS/DCPMS sequential donor catalyst system provides the highest possible level of amorphous copolymer in the bipolymer and at an acceptable level of MFR and homopolymer crystallinity.

Furthermore, because the highly isotactic components of the polymer crystallize first, a template is provided for the lesser stereoregular polypropylenes during subsequent crystallizations leading to undesirable lower flexural modulus. This behavior causes the lesser stereoregular polymers to be less affected by external nucleating agents. This becomes important when ICPs are colored with pigments, which can act as nucleating agents that cause additional crystallization. Since the amorphous segments of ICPs formed with sequential donor-produced propylene homopolymers are more resistant to nucleation by pigments, they retain a better balance of flexural modulus and impact resistance after pigmentation. This behavior also allows the ICPs of the present invention to be colored with a broader range of pigments without this deleterious effect, which is critical for many of the commercial end-use applications for which they may be incorporated, e.g., injection molded products.

The examples below further demonstrate the improved nature of materials formed in accordance with the methods of the present invention, in comparison to materials formed using methods employing a single electron donor.

As is apparent from the above data, the average stereoregularities of propylenes produced with a single CMMS donor/Catalyst B and the TEOS/DCPMS sequential donors/Catalyst A are similar. The average *meso* run length, which is the average isotactic sequence length between stereo defects is an excellent measure of polypropylene stereoregularity. The average *meso* run length for the CMMS donor in combination with Catalyst B was 207; the length of *meso* runs based on 12 observations ranged from 180 to 240. An average *meso* run of 207 was also observed in ICPs produced with the sequential TEOS/DCPMS donor system and Catalyst A; based on 4 observations ranging in average *meso* run Length (MRL) from 180 to 220.

The molecular weight distribution (M_w/M_n) for the single donor system with Catalyst B averaged 3.7 by GPC and ranged from 3.4 to 4.1. The average molecular weight distribution by GPC for the sequential donor system was 3.9, with values ranging from 3.3 to 4.6. Therefore, the molecular weight distribution

5   was slightly higher for the sequential donor formed polypropylene, while the average stereoregularities for the two donor/catalyst systems were similar. This change in molecular weight distribution, although apparently small, was manifested in the processing behaviors of the inventive and comparative ICPs. The peak injection pressure during injection molding was observed to be 6700 psi (46.16

10   MPa) for the CMMS single donor-produced ICPs. At the same final MFR, the TEOS/DCPMS sequential donor produced ICPs generated a peak injection pressure of only 5900 psi (40.65 MPa). It is well known to those skilled in the art that increasing the breadth of the molecular weight distribution of a polymer will improve processability during injection molding.

15

EXAMPLE 5

Each of the ICPs formed in accordance with Examples 4, above, were externally nucleated with sodium benzoate. As shown in Fig. 6 and Table 8, the ICPs formed using the sequential TEOS/DCPMS donor system of the present

20   invention are not affected to as great an extent by external nucleating sources (e.g., 12% or less difference) compared with ICPs formed via a single donor system which demonstrate greater than 27% difference.

TABLE 8

1% SECANT FLEXURAL MODULI BEFORE AND AFTER

NUCLEATION OF SINGLE AND SEQUENTIAL DONOR ICPS

	SEQUENTIAL DONORS			SINGLE DONORS*		
	% Xylene Solubles	1% secant Flexural Modulus (kpsi)		% Xylene Solubles	1% secant Flexural Modulus (kpsi)	
		un-nucleated	nucleated		un-nucleated	nucleated
1	19.90	172	192	12.26	155.7	207
2	16.91	177	195	14.71	155.7	197
3	14.6	182	205	13.59	155.7	208
4	16.1	177	200			
5	20.16	172	184			
6	18.57	179	197			
7	16.30	193	210			
8	16.57	166	181			
9	16.70	173	181			
10	16.95	167	184			
11	22.30	157	164			

* The data was averaged from a number of observations of a single grade.

Therefore, the balance between flexural moduli and impact resistance of the ICP formed via a sequential donor system will be better maintained regardless of the addition of nucleating agents and additives that can act as nucleating agents, such as pigments.

EXAMPLE 6

Each of the ICPs formed in accordance with Examples 4 and 5, above, were colored with gray and camel pigments as follows:

The samples for testing were molded on a 75 ton Van Dorn injection molding machine, using a mold with ASTM test specimens (ASTM D3641). The samples with pigments were dry blended in the pellet form prior to injection molding.

24

The superiority of ICPs formed using the sequential donor system of the present invention in maintaining impact properties after pigmentation compared to ICPs formed from a single donor system is shown by Figs. 7A and 7B, as well as in Table 9 below.

Table 9
(PHYSICAL PROPERTY EVALUATION)

Composition and Property	Sample #									
	1	2	3	4	5	6	7	8	9	10
Sequential Donors(wt.%)	100	98	98	98	98					
Single Donor (wt.%)						100	98	98	98	98
Medium misty grey pigment[1] (wt.%)		2					2			
Medium misty grey pigment[2] (wt.%)			2					2		
Medium camel pigment[3] (wt.%)				2					2	
Medium camel pigment[4] (wt.%)					2					2
MFR (dg/min)	35	35	35	35	35	35	35	35	35	35
1% Sec. Flexural Modulus (kpsi)	184	185	187	185	185	208	206	208	206	207
1% Tan. Flexural Modulus (kpsi)	190	191	193	192	190	214	212	215	213	207
HDT @ 66 psi (°C)	107	107	105	106	107	115	114	117	116	119
Gardner @ 23 °C	245	232	236	235	243	243	175	180	199	179
Gardner @ -29 °C	173	157	165	165	173	125	65	94	129	114
Notched Izod @ 23°C (ft-lbs/in)	1.32	1.38	1.33	1.50	1.55	0.86	0.78	0.75	0.84	0.83

1 denotes a carrier resin which is Linear Low Density Polyethylene
2 denotes a carrier resin which is Polypropylene
3 denotes a carrier resin which is Linear Low Density Polyethylene
4 denotes a carrier resin which is Polypropylene

The increased retention of impact properties allows ICPs produced by the sequential donor system of the present invention to be pigmented with a greater variety and quantity of pigments.

EXAMPLE 7

In the ICP process, the catalyst particles bearing the homopolymer component continue downstream to one of more gas phase reactors to produce in situ an ethylene propylene(E/P) copolymer with a predesigned ethylene content. The E/P copolymer has both a crystalline and an amorphous component, but only the amorphous component makes a significant contribution to the impact properties of the ICP. Inspite of the process and choice of magnesium chloride supported Ziegler-Natta base catalyst, the amorphous content of the E/P copolymer will increase as the total copolymer ethylene content diminishes. There can be some control exercised over the amount of amorphous E/P copolymer as a function of total ethylene content through a judicial choice of electron donor, as shown below for the CMMS and DCPMS single donor systems:

Table 10
(% Amorphous Ethylene/Propylene Copolymer
for Single Donors with Catalyst A)

Single Donor	Wt.% Amorphous E/P in total Bipolymer	Wt.% Ethylene in Total Bipolymer
CMMS	75.4	36
DCPMS	81.1	49
DCPMS	84.8	46

Although the DCPMS donor clearly leads to a higher amorphous copolymer content in the bipolymer, it cannot be used alone to produce an ICP because of the severe limitations placed upon the MFR of the polypropylene homopolymer component. The sequential donor concept has been found to alleviate this difficulty because the initial TEOS donor leads to a high MFR, which is averaged, and the DCPMS donor in the second reactor dominates TEOS sufficiently to produce a bipolymer downstream with characteristics more typically associated with that obtained from a single donor DCPMS process. This result is illustrated in Figure 8 and Table 11, below:

TABLE 11

% AMORPHOUS VERSUS % ETHYLENE IN BIPOLYMER AND CHOICE OF CATALYST/DONORS

#	Sequential Donors		Single Donor		Other ICPs*	
	% E in Bipolymer	% a-E/P in Bipolymer	% E in Bipolymer	% a-E/P in Bipolymer	% E in Bipolymer	% a-E/P in Bipolymer
1	44	82	59	75	56	79
2	41	76	58	75	57	70
3	39	74	62	73	35	77
4	49	83	55	77	64	62
5	50	82	57	75	50	70
6	33	83	58	76	51	70
7	56	78	61	72	50	75
8	53	85	52	74	45	74
9	45	82	72	58	56	70
10	46	82	69	59	52	76
11	49	87	66	72	49	74
12	60	69	68	68	53	78
13	43	86	53	73	50	80
14	38	81	60	67		
15	39	86	56	75		
16	43	85	56	77		
17	47	86	57	77		
18	41	83	63	74		
19	45	91	62	62		
20	48	87	64	60		
21	53	78	62	69		
22	45	77	60	69		
23	54	84	63	72		
24	53	85	59	73		
25	55	83	54	74		
26	54	81	59	74		
27	53	81	65	69		
28	51	80	61	69		
29	52	79	61	70		
30	67	71	60	71		
31	55	73				

5

TABLE 11 (cont'd)

% AMORPHOUS VERSUS % ETHYLENE IN BIPOLYMER AND

CHOICE OF CATALYST/DONORS

#	Sequential Donors		Single Donor		Other ICPs*	
	% E in Bipolymer	% a-E/P in Bipolymer	% E in Bipolymer	% a-E/P in Bipolymer	% E in Bipolymer	% a-E/P in Bipolymer
32	60	78				
33	69	58				
34	57	85				
35	59	82				
36	59	81				
37	58	84				
38	54	77				
39	57	77				
40	63	81				
41	62	79				
42	55	83				
43	55	79				
44	59	77				
45	58	80				
46	58	79				

* ICPs made from methods other than those of the present invention.
Samples 1 and 2 are ICPs sold by Himont.
Sample 3 is an ICP sold by Amoco Chemical Company.
Samples 4, 9, 10 and 12 are ICPs sold by Mitsubishi Chemical Company, Ltd.
Samples 5 and 6 are sold by Tonen.
Samples 7, 8 and 11 are ICPs sold by Aristech.
Sample 13 is an ICP sold by Genesis.

Fig. 8 plots the total copolymer wt.% ethylene against wt.% amorphous

copolymer for ICPs produced by sequential addition of electron donors

(TEOS/DCPMS) and single (CMMS) donors, respectively. For comparison

purposes, Fig. 8 also has data, i.e., samples 1-13, generated from commercially

available ICPs made by processes different from that of the present invention. The

majority of ICPs produced by the sequential addition of donors contained more

than 80 wt.% amorphous copolymer. Fig. 8 further demonstrates the previous

statement that the wt.% amorphous copolymer increases as the total copolymer

wt.% ethylene decreases. Even at a 60 wt.% ethylene content (total copolymer

wt.%), the amorphous copolymer content was 75 to 80% for the sequential
donor-prepared ICP, as opposed to only 70% for the single CMMS donor-
prepared ICPs. The other ICPs of samples 1-13 give results similar to that
observed for a single donor system. Fig. 8 also shows that the wt.% amorphous

5   copolymer for the sequential TEOS/DCPMS is similar to that produced by use of a
DCPMS donor, alone. The increased wt.% amorphous copolymer for the
sequential donor-produced ICPs leads to a better balance between flexural moduli
and impact strength. A sodium benzoate-nucleated ICP with 12 wt.% xylene
solubles and prepared with a single CMMS donor and Catalyst B displays a 1%

10   secant flexural modulus of 210 ± 5 (kpsi) and a Gardner impact strength at -29°C
of 120 ± 26 inch lbs. The corresponding nucleated ICP prepared by sequential
addition of electron donors and 16 wt.% xylene solubles displays a 1% secant
flexural modulus of 184 ± 5 (kpsi) and a Gardner impact strength at -29°C of 168
± 11 inch lbs. The following equation can be used to predict 1% secant flexural

15   moduli for nucleated ICPs prepared with the single donor system:

$$1\% \text{ Secant Flexural Modulus (kpsi)} = -4.90 \text{ (wt.\% xylene solubles)} + 248.3 \qquad \text{(Eq. C)}$$

The following results are obtained for 12 and 16% xylene solubles:

20

Table 12

% Xylene Solubles	Predicted 1% Secant Flexural Modulus (kpsi)	Observed 1% Secant Flexural Modulus (kpsi)
12	190	210 (single donor)
16	170	184 (sequential donor)

This exercise demonstrates that the 1% secant flexural moduli are
comparable for the nucleated ICPs prepared with single and sequential donors,
respectively.

30   The impact strengths, however, differ substantially with the sequential
donor prepared ICP having a Gardner Impact Strength at -29°C of 168 inch

pounds, while the comparable single donor system has a Gardner Impact Strength at -29°C of only 120 inch pounds. This difference in impact strengths is also demonstrated in Table 9. The sequential donor catalyst system allows more bipolymer to be incorporated into an ICP with an accompanying higher amount of amorphous E/P without sacrificing the 1% secant flexural modulus.

The amorphous content of the bipolymer formed according to the present invention may be between 75-100%, preferably between 80-100%, at an ethylene content of 60% or greater in the bipolymer. At lower ethylene content the amorphous content will be between 82-100%, preferably between 84-100%, more preferably between 86-100%. In another embodiment the amorphous content of the bipolymer is between 82-98%, preferably 84-98%, more preferably 85-98%, and most preferably 86-98%.

Physical Property Measurements

- **Melt Flow Rate (MFR)**

MFR is measured according to ASTM D1238 test method, at 230°C and 2.16 kg load, and is expressed as dg/min or g/ 10 min.

- **Flexural Modulus**

The flexural modulus is obtained according to ASTM D790A, with a crosshead speed of 1.27 mm/min, and a support span of 50.8 mm, using an Instron machine.

- **Gardner Impact Strength**

The Gardner Impact Strength was measured according ASTM D3029, Method G, Procedure GC, at -29°C and 23°C, on 90 mm diameter and 3.175 mm thickness disks.

- **Heat Deflection Temperature**

The heat deflection temperature (HDT) is measured according to ASTM D 648, and under a load of 66 psi, using the equipment made by Ceast Corp.,

- **Notched Izod Impact Strength**

        The room temperature notched izod impact strength (RTNI) is measured
according to ASTM D256 test method. The impact strength equipment is made by
5   Empire Technologies Inc.

- **Procedure for Xylene Solubles and Insolubles of Impact Copolymers of Polypropylene**

        The procedure consists of pressing polymer resin in the form of pellets into
10   a pad by melt pressing at 210°C for 1 minute and cooling to room temperature in 1
minute. A 2 gram sample from the pad is weighed and dissolved in xylene at
135°C. After the polymer is dissolved completely, the heat source is removed and
allowed to cool spontaneously overnight. The precipitated or solidified polymer is
filtered, washed thoroughly with xylene, dried and weighed. The solidified portion
15   thus obtained is represented as xylene insolubles. The filtrate containing the
soluble polymer is concentrated by removing xylene under vacuum overnight. The
polymer thus obtained is washed with a small amount of acetone and dried. The
weight of the polymer thus obtained is represented as xylene solubles at room
temperature.
20   While preferred embodiments in accordance with the invention have been
shown and described, it is to be clearly understood that the same are susceptible to
numerous changes apparent to one of ordinary skill in the art. Therefore, the
invention should not be deemed to be limited to the details shown and described
above, but should be considered to include all changes and modifications that come
25   within the scope of the appended claims.

CLAIMS

We claim:

1.   A method of forming a high impact copolymer comprising:

subjecting an α-olefin monomer to an initial polymerization, in the presence

of a first electron donor material and a first catalyst to form a polymer product;

subjecting said polymer product to a subsequent reaction, in the presence of

a second electron donor material and a second catalyst, thereby forming said α-

olefin homopolymer; wherein said second donor material is more stereoregulating

than said first electron donor material and said second electron donor material

dominates said first electron donor material; and

polymerizing a copolymer in the presence of said α-olefin homopolymer;

thereby forming said high impact copolymer;

preferably wherein said α-olefin monomer is selected from the group

consisting of: propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-

nonene, and 1-decene;

preferaably wherein said first and second electron donor materials are any

organic silicon compounds;

2.   The method of claim 1, wherein said first electron donor material is

tetraethoxy silane and said second electron donor material is

dicyclopentydimethoxysilane, and wherein said copolymer is selected from any

ethylene/α-olefin copolymer.

3.   The method of claim 1, wherein said first and second catalysts are

either the same or different from one another.

4.   The method of any of the preceeding claims, wherein said

copolymer is an ethylene/α-olefin copolymer having a weight ratio of ethylene to

α-olefin in an amount between 20:80 to 80:20, and wherein the ethylene content

of said ethylene/α-olefin copolymer is in the range between 1 to 80 wt.%.

5.   A high impact copolymer having a bipolymer component, said bipolymer component being at least 80% amorphous phase with the remainder being crystalline, said copolymer having an overall ethylene content in the range between 60 to 80%.

6.   The high impact copolymer of claim 5, further having a flexural modulus in the substantial absence of a nucleating agent at least 10% greater than that described by the general equation:

1% secant flexural modulus = -3.00 (wt.% xylene solubles) + 209.5

wherein wt.% xylene solubles is the wt.% of said high impact copolymer chain which is soluble in xylene at 21-25°C, and wherein said high impact copolymer has a melt flow rate in the range between 10 to 150.

7.   The copolymer of claim 6, further comprising 2 wt.% pigment and carrier, based on the combined weight of said copolymer, wherein the pigmented copolymer retains at least 95% of the impact resistance of non-pigmented copolymer at both 25°C and -29°C.

8.   A high impact copolymer comprising an ethylene/α-olefin copolymer component that contains at least 75% amorphous phase, with the remainder being crystalline, said copolymer having an overall ethylene content is 60% or greater.

9.   A high impact copolymer which comprises an ethylene/α-olefin copolymer component that contains at least between 82 to 100 wt.%, preferably between 84 to 100 wt.%, more preferably between 86 to 100 wt.% amorphous phase ethylene-α-olefin and between 0 to 18 wt.%, preferably between 0 to 16 wt.%, more preferably between 0 to 14 wt.% crystalline phase ethylene-α-olefin,

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wherein the ethylene content in said ethylene/α-olefin copolymer is 60 wt.% or less.

10.   The copolymer of claim 9 further comprises pigment additives, whereby said high impact copolymer maintains a substantially constant Gardner impact at -29°C.

11.   The copolymer of claim 9, wherein said high impact copolymer retains 95% or better of its Gardner impact at 25 and -29°C after 2 wt.% pigmentation with carriers of poly(α-olefin) or linear low density polyethylene and with different colors.

12.   The copolymer of claim 9, wherein said high impact copolymer has a flexural modulus in the substantial absence of a nucleating agent, at least 10%, preferably 15% greater than that described by the general equation:

1% secant flexural modulus = - 3.00 (wt.% xylene solubles) + 209.5

wherein wt.% xylene solubles is the wt.% of said high impact copolymer chain which is soluble in xylene at 21-25°C, and wherein said high impact copolymer has a melt flow rate in the range between 10 to 150; and

preferably, wherein said high impact copolymer includes an ethylene α-olefin copolymer containing at least 82% or greater amorphous phase

HYDROGEN RESPONSE FOR DCPMS AND TEOS
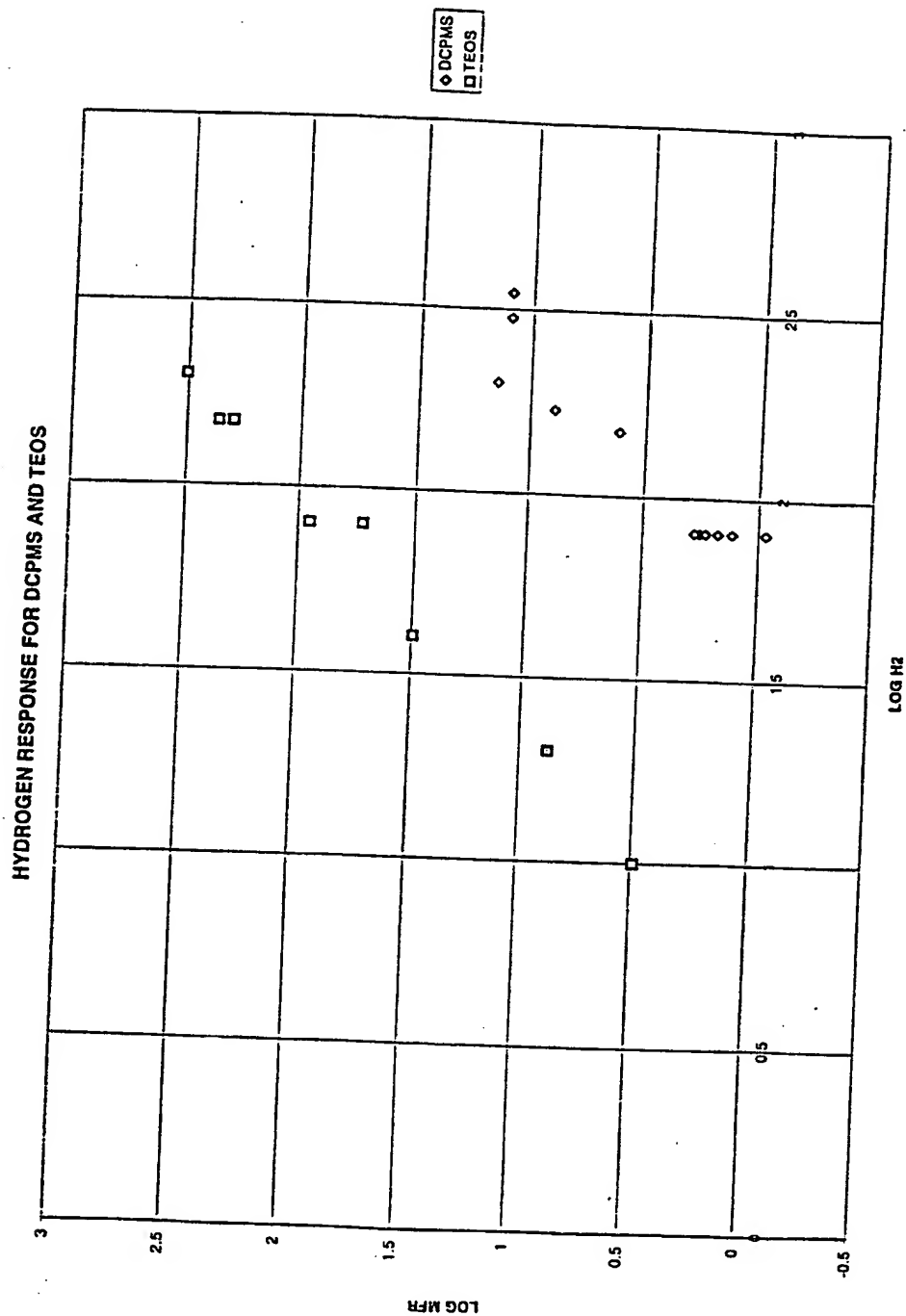
TEOS/DCPMS AND PTES/DCPMS MIXED DONOR RATIOS VERSUS MFR
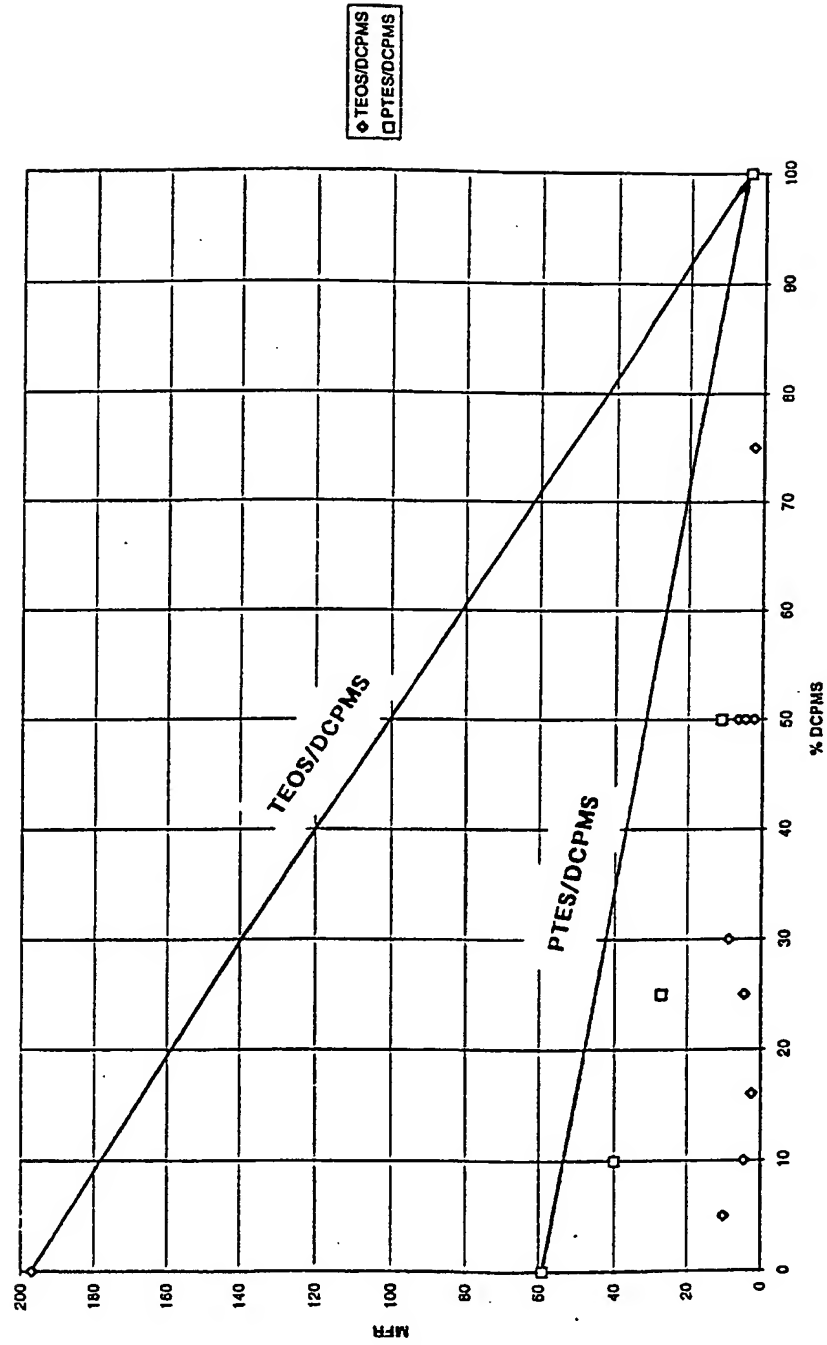
THE LINES REPRESENT THE EXPECTED BEHAVIOR FOR A LINEAR RELATIONSHIP

HEAT OF FUSION VS. % DCPMS

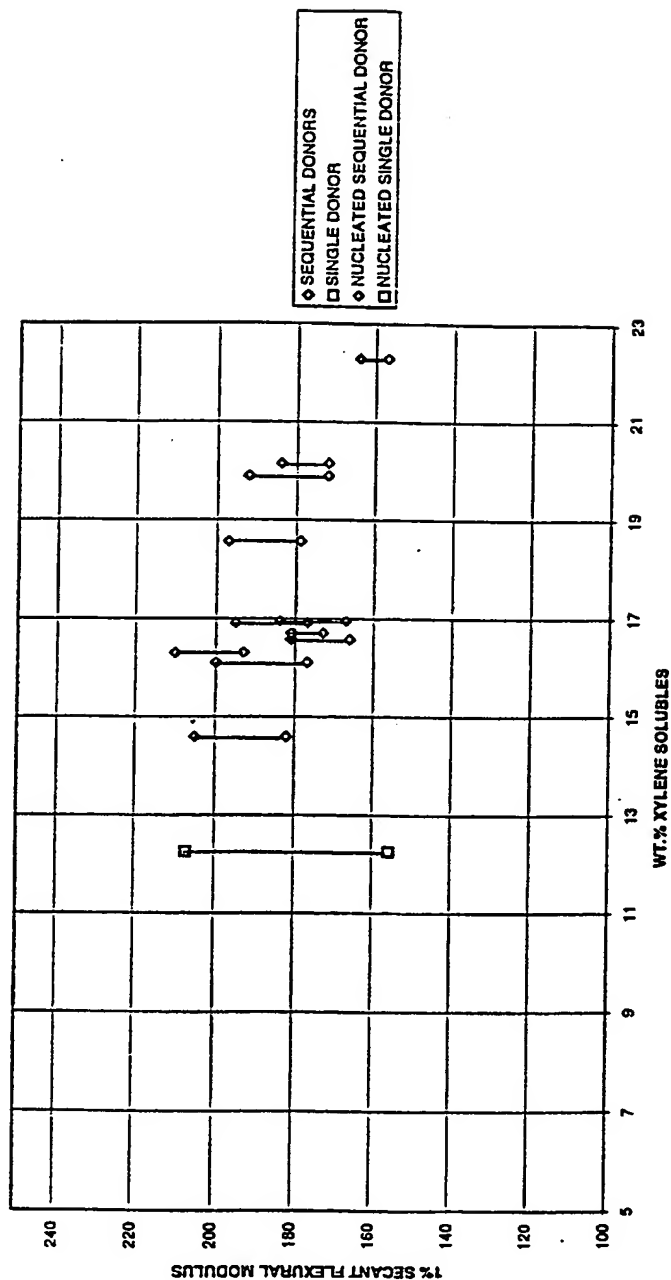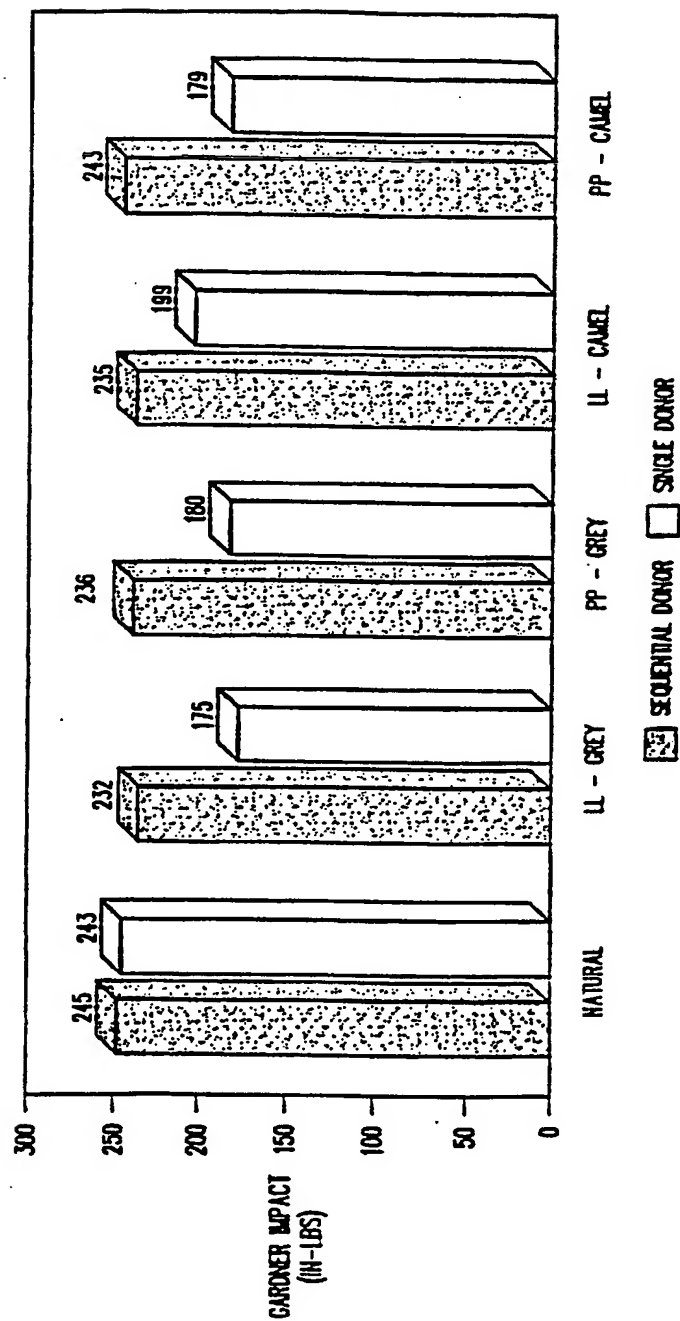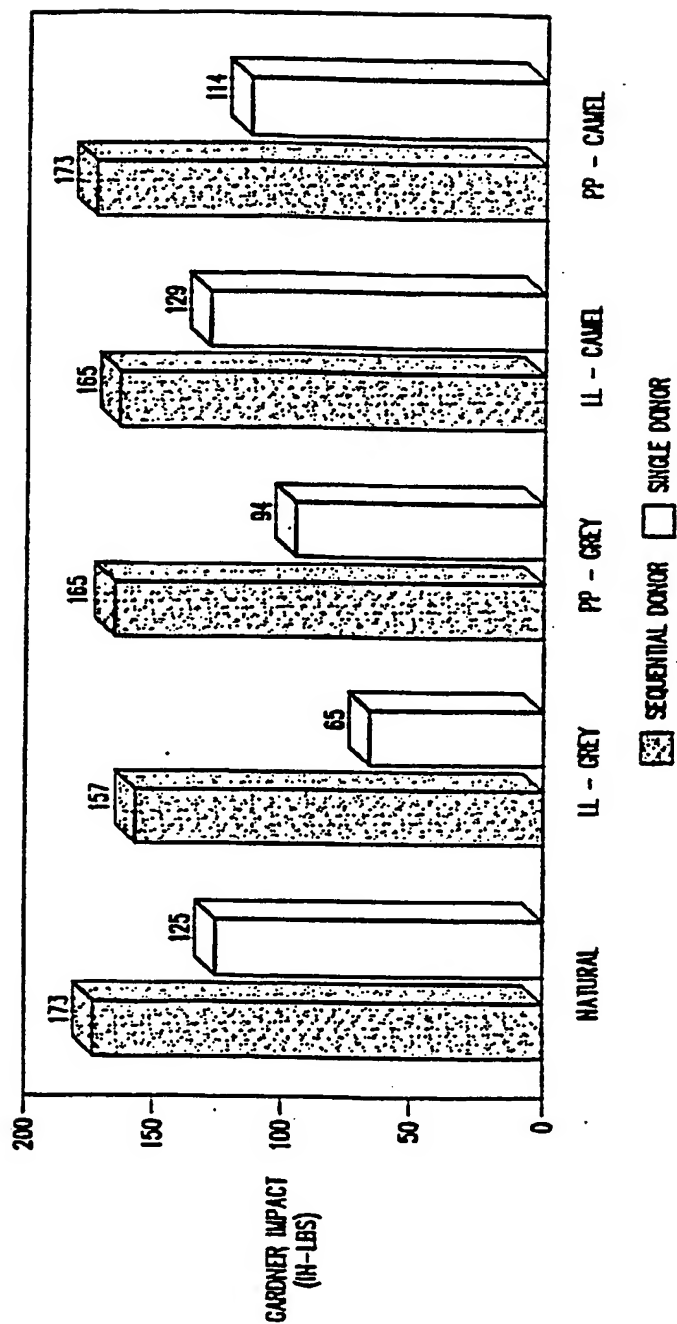STEREOREGULARITY AND IT'S DISTRIBUTION WITH SEQUENTIAL & SINGLE DONORS

DONOR B
MRL = 200

DONOR A
MRL = 150–180

DONOR C
MRL = 400

SEQUENTIAL DONORS
MRL = 200

STEREOREGULARITY [MESO RUN LENGTH (MRL)]

SINGLE VS. SEQUENTIAL DONORS

SINGLE DONOR
SEQUENTIAL DONOR

WT. % XYLENE SOLUBLES

1% SECANT FLEXURAL MODULUS

EFFECT OF NUCLEATION - SINGLE vs. SEQUENTIAL DONORS

GARDNER IMPACT (IN-LBS)

NATURAL: 243, 245
LL - GREY: 175, 232
PP - GREY: 180, 236
LL - CAMEL: 199, 235
PP - CAMEL: 179, 243

SEQUENTIAL DONOR   SINGLE DONOR

% Amorphous E/P for Sequential versus Single Donors

Legend: ◇ SEQUENTIAL DONORS ▫ SINGLE DONORS △ NON-EXXON ICPs

(54) Title: HIGH IMPACT, FLEXURAL MODULI POLYMERIC MATERIALS FORMED USING SEQUENTIAL DONORS

(57) Abstract

A method of forming high impact copolymer having a high degree of crystallinity and a melt flow rate of at least 10 to 150. The method preferably comprising: subjecting the α–olefin monomer to an initial polymerization, in the presence of a first electron donor material and a first catalyst to form a polymer product; subjecting the polymer product to a subsequent polymerization, in the presence of a second electron donor material and a second catalyst, thereby forming the α–olefin homopolymer; wherein the second donor material is more stereoregulating than the first electron donor material and the second electron donor material dominates the first electron donor material; and polymerizing a copolymer in the presence of the α–olefin homopolymer; thereby forming a high impact copolymer. The first and second catalysts may be the same or different. The copolymer portion of the high impact copolymer will have an unexpected high amorphous phase content.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C08F297/08   C08L23/12   C08L23/16   C08L53/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C08F   C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 95 21203 A (EXXON CHEMICAL PATENTS INC) 10 August 1995 see page 3, line 21 - page 5, line 14 see page 7, line 17 - page 10, line 8 see page 11, line 18 - page 12, line 19 see page 21, line 10 - page 22, line 11; claims; examples ---	1,2,4
Y	GB 2 035 343 A (MITSUBISHI PETROCHEMICAL CO) 18 June 1980 see the whole document ---	1,2,4
X	US 4 493 923 A (J. DOUGLAS MCCULLOUGH, JR.) 15 January 1985 see claim 1 ---	5,8,9
	-/--	

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 June 1999	07. 07. 1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Kaumann, E

Form PCT/ISA/210 (second sheet) (July 1992)

2

page 1 of 2

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 552 482 A (BERTA DOMINIC A) 3 September 1996 see column 4, line 44 - line 51; claim 1 ---	5-7
X	EP 0 490 353 A (UNION CARBIDE CHEM PLASTIC) 17 June 1992 see claim 1 ---	9-12
X	US 5 338 801 A (EPPERT JR STANLEY E) 16 August 1994 see claims 1-3 ---	9-12
X	US 5 455 303 A (PANAGOPOULOS JR GEORGE ET AL) 3 October 1995 see claims -----	5-8

2

INTERNATIONAL SEARCH REPORT

Box I   Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [X] Claims Nos.:   3
because they relate to subject matter not required to be searched by this Authority, namely:

> The electron donor, which forms part of the catalyst system, has to be different in the first and the second reaction step as an essential feature

2. [X] Claims Nos.:   3
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

> The electron donor, which forms part of the catalyst system, has to be different in the first and the second reaction step as an essential feature.

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II   Observations where unity of Invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

> see additional sheet

1. [X] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest   [ ] The additional search fees were accompanied by the applicant's protest.

[X] No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1998)

FURTHER INFORMATION CONTINUED FROM   PCT/ISA/ 210

This International Searching Authority found multiple (groups of)
inventions in this international application, as follows:

1. Claims: 1-4

> Subject-matter of claims 1 - 4 is a polymerization process,
> which is carried out in three steps. In steps one and two, a
> homo-alpha-olefin polymer having blocks of different degrees
> of stereoregularity, caused by the use of different electron
> donors, is formed and in step three, a copolymer is formed
> in the presence of the previously prepared homopolymer.

2. Claims: 5-12

> Subject-matter of claim 5 - 12 is a high impact copolymer,
> which comprises a binary copolymer having a high content of
> amorphous phase and an overall

INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9521203	A	10-08-1995	AT	166074 T	15-05-1998
			CA	2182717 A	10-08-1995
			CN	1156999 A	13-08-1997
			DE	69502480 D	18-06-1998
			DE	69502480 T	10-12-1998
			EP	0743960 A	27-11-1996
			ES	2119401 T	01-10-1998
			FI	963081 A	03-10-1996
			JP	9508657 T	02-09-1997
			NO	963236 A	25-09-1996
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			JP	55071712 A	30-05-1980
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			DE	2946984 A	04-06-1980
			NL	7908507 A,C	28-05-1980
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US 5552482	A	03-09-1996	EP	0767209 A	09-04-1997
			JP	9118795 A	06-05-1997
EP 0490353	A	17-06-1992	US	5173536 A	22-12-1992
			AT	123298 T	15-06-1995
			CA	2057471 A	12-06-1992
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			DE	69110115 T	19-10-1995
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			KR	134767 B	20-04-1998
US 5338801	A	16-08-1994	AT	158329 T	15-10-1997
			AU	675874 B	20-02-1997
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US 5455303	A	03-10-1995	AT	172221 T	15-10-1998
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			CN	1118361 A	13-03-1996
			DE	69505311 D	19-11-1998
			DE	69505311 T	08-04-1999
			EP	0688820 A	27-12-1995
			ES	2125520 T	01-03-1999
			FI	953046 A	21-12-1995
			JP	8003385 A	09-01-1996
			NO	952446 A	21-12-1995

(54) Title: CATALYST SYSTEM CONTAINING A SOLID TITANIUM COMPONENT FOR THE STEREOREGULATION OF POLYOLEFINS

(57) Abstract

The present invention provides a catalyst system that exhibits unprecedented control of stereoregularity and generates an olefin polymer product having low to moderate crystallinity. The catalyst system includes (a) a solid titanium catalyst component, (b) a mixture comprised of diethylaluminum chloride and another organoaluminum compound as co-catalyst, and (c) an alkylsilane electron donor. When employed in the polymerization of propylene, the system exhibits control over the polymer stereoregularity and generation of undesirable atactic polymers resulting in the preparation of a novel polypropylene polymer of low to moderate crystallinity.

CATALYST SYSTEM CONTAINING A SOLID TITANIUM COMPONENT FOR THE STEREOREGULATION OF POLYOLEFINS

5

FIELD OF THE INVENTION

The present invention relates to a catalyst system and an olefin polymerization that results in an olefin polymer composition demonstrating

10   moderate to low crystallinity and relatively low amounts of by-product amorphous polymer. The low proportion of amorphous polymers in the instant polyolefins enables continuous reactor preparation of such resins without the accompanying production difficulties generally associated with polyolefin compositions of moderate to low crystallinity.

15

BACKGROUND OF THE INVENTION

Catalyst systems for the polymerization of olefins are well known in the art. Typically, these systems include a Ziegler-Natta type polymerization

20   catalyst component; a co-catalyst, usually an organoaluminum compound; and an electron donor compound. Examples of such catalyst systems are shown in U. S. Patent Numbers: 5,066,738 (Ewen); 4,990,479 (Ishimaru); 4,990,477 (Kioka); and 4,970,186 (Terano) the entire disclosures of which U. S. patents are hereby incorporated by reference for purposes of US patent practice. These

25   are a few of many issued patents and other prior art relating to Ziegler-Natta catalyst and catalyst systems designed primarily for the polymerization of olefins.

Ziegler-Natta type polymerization catalyst components are basically a

30   complex derived from a halide of a transition metal, for example, titanium, chromium, or vanadium with a metal hydride and/or a metal alkyl that is typically an organoalumium compound. The catalyst is usually comprised of a titanium halide composition supported on a magnesium compound complexed with an alkylaluminum compound. There have been generations of these

35   catalysts as well as new polymerization processes developed in the prior art. One of the newer generations of these catalyst components is disclosed in the U. S. Patent number 4,970,180, cited above, and in U. S. Patent numbers:

2

4,847,227; 4,839,321; 4,829,037; 4,816,433 and 4,686,200, all of which are
owned by the TOHO Titanium Company of Tokyo, Japan and the entire
disclosures of which are hereby incorporated by reference for purposes of US
patent practice.

5

In addition to the improvement or development of new Ziegler-Natta
catalyst components and polymerization processes, the discovery of more
appropriate co-catalysts and/or electron donors to accompany these new
generations of titanium-supported catalyst systems have resulted in improved
10   quality control of the polyolefin polymer product. The co-catalysts that work
well with the newer generations of solid titanium-supported catalysts are
organoaluminum compounds, most typically the alkylaluminum series such as
triethylaluminum ("TEAl"), diethyl-aluminum chloride ("DEAC") and
triisobutylaluminum. Examples of other useful organoaluminum compounds
15   include alkylaluminum dihalides and trialkoxyaluminum compounds. Mixtures
of these prior art organoaluminum co-catalysts are disclosed in the prior art as
in U. S. Patents 4,678,768 (Fujita et al.); 4,716,206 (Fujita et al.); and
4,634,687 (Fujita et al.), all of which teach co-catalyst mixtures of DEAC and
TEAl for use in magnesium supported TiCl4 catalyst component systems.

20

It is known that the levels of stereoregularity achieved by classical
Ziegler-Natta catalyst recipes containing titanium chlorides and various co-
catalysts can be controlled by the choice and level of the type of electron donor.
An electron donor compound is generally used along with catalyst components
25   in olefin polymerization reactions to increase the stereoregularity of the polymer
while concurrently decreasing the production of atactic or amorphous polymers
thereby ensuring higher crystallinity of the polyolefin product. Various types of
external donors, used in polypropylene catalyst recipes to control the level of
stereoregularity, include alkyl, alkoxy (or even chlorine) substituted silane
30   compounds (U. S. Patent 5,206,198), benzoic acid esters (U. S. Patents
4,463,102; 4,716,206; 4,678,768; and 4,246,136), aromatic esters containing
nitrogen atoms (U. S. Patents 4,716,206 and 4,634,687), alkyl substituted
piperidines (U. S. Patent 4,634,687), and aliphatic amines   (U. S. Patent
4,634,687). Discovery of an appropriate type of electron donor can lead to
35   significant increases in catalyst efficiency as well as improved control of the
stereoregularity of the desired polymer product and, if desired, control of other
properties of the polymer polyolefin product such as molecular weight

distribution ("MWD") and melt flow. Likewise, discovery of a specific group of electron donors in combination with a solid titanium-supported component/co-catalyst system could result in control of the percentage heptane insolubles (% HI) of a desired polyolefin polymer product by maintaining

5   control over the formation of undesirable by-product amorphous atactic polymer. The success of the various donors is generally established by determining the percent of heptane insolubles, "% HI" (U. S. Patent numbers 4,246,136; 4,335,015; 4,634,687; 4,678,768; 4,716,206; and 4,463,102). The % HI is also often used as an index of the isotacticity of a crystalline

10   polypropylene. Throughout this specification, the level of polypropylene isotacticity shall be defined by the average undisturbed stereoregular run lengths of *meso* diads in the crystalline fraction of the subject polyolefin polymers composition. The % HI shall be used to indicate the level of the crystalline fraction of a polypropylene composition.

15

Specified % HI levels are generally important in processing of polypropylene polymer compositions as the atactic polymer contained therein will act as a processing aid. This is particularly true for processes that make polypropylene films. A particular example is oriented polypropylene films made

20   by a process called the tenter frame. An example where low levels of atactic polypropylene are desirable are in molding applications which require good heat resistance as reflected by a higher heat distortion temperature ("HDT"). Reducing atactic polypropylene levels in the polypropylene composition will lead to an increase in the heat distortion temperature of the resulting molded

25   articles. It is clearly advantageous to have a polypropylene composition that is both easily processable yet can also be designed to contain relatively low levels of atactic polypropylene so as to increase the heat distortion characteristics of manufactured articles.

30   The present invention involves the discovery of a certain catalyst system that can be used to control the stereoregularity of polyolefin polymers and thereby achieve polymer compositions of moderate to low crystallinity which contain relatively low levels of amorphous or atactic polymer. It has been surprisingly found that a (1) a particular organoaluminum co-catalyst mixture

35   and (2) a specific group of silane compounds serving as electron donors in combination with a $TiCl_4$ supported catalyst component results in a catalyst system which can generate a polyolefin composition having a low to moderate

4

crystallinity and an unexpectedly lower amount of by-product heptane soluble
amorphous polymer than ordinarily generated in the preparation of olefin
polymer compositions of comparable crystallinity. The instant catalyst system
enables the practice of a polymerization process exhibiting an improved control

5   of the stereoregularity of the polymer product than otherwise provided with
catalyst systems of the prior art.

SUMMARY OF THE INVENTION

10   The present invention provides a catalyst system for the polymerization
of olefins which system includes a combination of a solid titanium component
with a specific composition comprised of an organoaluminum co-catalyst
mixture and an organosilane electron donor compound, resulting in unexpected
and significant control of the properties of the polymer product generated

15   therewith. The catalyst component is a solid titanium component which
contains magnesium, titanium, halogen, and an internal electron donor as
essential elements. The organoaluminum co-catalyst mixture is comprised of
diethyl aluminum chloride ("DEAC") in an amount of 3 to 75 mole percent and
at least one other organoaluminum compound such as triethylaluminum, in an

20   amount of 97 to 25 mole percent. The external electron donor is an
organosilane compound such as methylcyclohexyl dimethoxysilane ("MCMS"),
or dicyclopentyldimethoxysilane ("DCPMS"). The present catalyst system is
used in polymerization processes to generate a novel polyolefin polymer
composition of moderate to low (relatively low) crystallinity having lower than

25   expected atactic (amorphous) polymer formation as reflected in lower heptane
solubles in the polymer than comparable prior art polyolefin compositions.

        The invention also provides for a process for the polymerization of
olefins. The process comprises: (a) providing a catalyst system comprised of (i)

30   a solid titanium catalyst component comprising magnesium, titanium, halogen,
and an internal electron donor; (ii) a co-catalyst comprised of a mixture of
diethylaluminum chloride in an amount of 3   to 75 mole percent and at least
one other organoaluminum compound, such as triethylaluminum, in an amount
of 97 to 25 mole percent; and   (iii) an external organosilane electron donor

35   such as MCMS or DCPMS; (b) introducing the catalyst system into a
polymerization reaction zone containing additional amounts of (i) the
organoaluminum co-catalyst mixture, (ii) the external organosilane electron

donor, and (iii) olefin monomer wherein polymerization of the monomer takes place. The process may include the optional step of prepolymerizing the catalyst system by contacting a small amount of olefin monomer with the catalyst system prior to entry into the reaction zone. The instant polymerization

5   process further includes the steps of (c) maintaining the mole percent of DEAC in the reaction zone between about 3 to 75 mole percent of the total amount of organoaluminum co-catalyst employed, and (d) withdrawing from the reaction zone a polyolefin composition containing heptane soluble polymer in an amount of 2 to 10 weight percent of total polyolefin polymer. It is further preferable

10   that the Al/Si mole ratio in the reaction zone be maintained within the range of from 5 to 1000.

         Up until the present invention, it has been assumed in the polymerization of propylene, that there is a consistently proportionate relationship between the

15   amount of atactic amorphous polypropylene in the catalyst generated polyolefin composition and the level of stereoregularity in the crystalline portion of that composition (see prior art patents cited above). In other words, the higher the stereoregularity in terms of unperturbed stereoregular sequences in the crystalline (heptane insoluble) segment, the lower the amount of amorphous or

20   atactic polymer formation, and vice versa. The development of the present invention goes beyond that assumption through the discovery of a polypropylene synthesis that leads to a composition that has a crystalline (heptane insoluble) portion of moderate to low crystallinity, but without a corresponding proportionate increase in the formation of atactic polypropylene.

25   This unexpected reduction in atactic polypropylene formation in the instant polypropylene compositions of relatively low, or moderate to low, crystallinity is measured by a generally lower heptane soluble portion than otherwise measured in comparable prior art polypropylenes of moderate to low crystallinity.

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         The above described unexpected results of the present invention are due to the instant catalyst system recipes that can be designed to yield polypropylene compositions having crystalline polypropylene portions of low stereoregularity accompanied by lower than expected amorphous polymer

35   formation as measured by differentials in the heptane soluble portions of the respective polypropylene compositions. By use of the present catalyst system in the polymerization of propylene, it has been found that the stereoregularity of

6

the polymer chains can be controlled and manipulated to the extent of achieving a polyolefin composition having relatively higher portions of low or moderately crystalline polymers and a lower than expected amount of amorphous polypropylene than demonstrated by polypropylenes of comparable similar

5   crystallinity in the prior art.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a characteristic diagram illustrating the correlation between

10   heats of fusion and corresponding average *meso* run lengths of the crystalline portions of the series of polypropylene compositions.

Figure 2 is the plot of Figure 1 further illustrating the crystallinity region of interest for the polypropylene compositions of the present invention.

15

Figure 3 is a characteristic diagram illustrating and highlighting the correlation between the heats of fusion, as a measure of crystallinity, and corresponding heptane insoluble contents of polypropylene compositions of the prior art and the present invention.

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Figure 4 is an expanded view of the highlighted compositions of the present invention shown in Figure 3.

Figure 5 is a characteristic diagram illustrating and highlighting the

25   correlation between the average *meso* run lengths, as an indicator of crystallinity, versus percentage of heptane insolubles in polypropylene compositions of the prior art and of the present invention.

Figure 6 is an expanded view of the highlighted compositions of the

30   present invention shown in Figure 5.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to an olefin polymerization catalyst

35   system which is the combination of (i) a solid titanium-supported Ziegler-Natta catalyst component; (ii) a particular mixture of organoaluminum compounds as co-catalysts; and (iii) an external organosilane electron donor for use in the

polymerization of propylene. This catalyst system is based on the discovery that the use of certain co-catalyst mixtures in combination with silane donors are factors controlling the isotacticity of polypropylene compositions as measured by the heptane insoluble portions of same.

5

As used herein isotacticity and isotactic level refers to the average run length of unperturbed stereoregular so-called "*meso* diad sequences". This is the length of the *meso* diad sequences that are terminated by some type of "stereo-defect" in the recurring stereoregular sequence. Theoretically predicted

10   stereo-defects that disrupt continuous *meso* diad sequences are shown as follows: ("1" is used to designate one type of stereochemical configuration, and "0" is used to designate the other, and only second, type of stereochemical configuration. A *meso* diad sequence can be either "00" or "11". A *racemic* diad can either be "01" or "10".).

8

meso diad   *racemic diad*

↓   ↓

∩   ∩

5   –000000000000000010000000000000000–

– *mmmmmmmmmmmmmmmmrrmmmmmmmmmmmmmmm*–

–0000000000000000110000000000000000–

–*mmmmmmmmmmmmmmmmrmrmmmmmmmmmmmmmmm*–

10

–0000000000000001110000000000000000–

–*mmmmmmmmmmmmmmmmrmmmrmmmmmmmmmmmmmmm*–

–00000000000000001111111111111111–

15   –*mmmmmmmmmmmmmmmrmmmmmmmmmmmmmm*–

–00000101010101010101010101010100000–

–*mmmmmrrrrrrrrrrrrrrrrrrrrrrrrrrmmmmm*–

20   –00000000000000010100000000000000–

–*mmmmmmmmmmmmmmmmrrrmmmmmmmmmmmmmmm*–

–0000000000000001011111111111111111–

–*mmmmmmmmmmmmmmmmrrrmmmmmmmmmmmmmm*–

25

–0000000000000001010111111111111111–

–*mmmmmmmmmmmmmmmmrrrrmmmmmmmmmmmmm*–

The above stereo-defects can terminate runs of like configurational

30   (*meso*) diad sequences. It is to be appreciated that each type of stereo-defect

begins with the sequence, *mmmr*, and ends with the sequence, *rmmm*. The

frequency of these stereo-defects will determine the run lengths of the *meso*

diad sequences. An average *meso* run length per 10,000 repeat units can be

determined from carbon 13 NMR methyl pentad data from a heptane insoluble

35   polypropylene fraction and the following relationship:

"Average *Meso* run length" = $2/[mmmr]$

where [*mmmr*], determined from carbon 13 NMR analysis, is equal to *mmmr* plus *rmmm*. The technique for generating NMR methyl pentad data to describe crystallinity is given in U. S. Patent number 4,522,994, the entire disclosure of
5   which is incorporated by reference herein for purposes of US patent practice.

Another more traditional method for evaluating polypropylene crystallinity is the percent heptane insolubles (% HI). Atactic polypropylenes are produced concurrently by the catalysts and polymerization processes that
10   produce these polypropylene compositions. Atactic polypropylene has no stereoregularity and, consequently, it is amorphous and has no melting point. Atactic polypropylene, in contrast to crystalline polypropylene, is soluble in most aromatic solvents (including heptane) at room temperature and can be extracted from crystalline polypropylenes with aliphatic hydrocarbon solvents
15   near their boiling point. Historically, there has been a systematic relationship between % HI and polypropylene crystallinity. Consequently, % HI has often been used in literature and patents as a method to establish the level of polypropylene crystallinity. Values for % HI generally range from percentages in the mid 80s to the upper 90s with the higher % HI levels usually indicating
20   higher levels of crystallinity in the heptane insoluble portion of the polymer composition.

The heart of the present invention resides in the use of critical amounts of diethylaluminum chloride in the catalyst system to achieve a polyolefin
25   polymer having desirable *meso* diad (or recurring stereoregular sequences) resulting in relatively lower crystallinity in the polyolefin without an increase in the concurrent formation of undesirable atactic (amorphous) polyolefin. This catalyst system enables the preparation of a more processable polyolefin composition because of the relatively lower % heptane insolubles which
30   produces a polymer composition with an unexpected lower content of undesirable amorphous polymer. This latter feature reduces the "stickiness" associated with atactic portions of the polyolefin and the likelihood of "fouling" in polymerization reaction systems, particularly in bulk or continuous processes.

35   In particular, the instant catalyst system generates a novel polypropylene composition having adequately and consistently distributed perturbations in the polymers thereof resulting in a composition of relatively low crystallinity, and

low amounts of amorphous (atactic) polypropylene, as measured by a relatively
higher heptane insolubility (% HI) than would ordinarily be expected from prior
art polyolefins of comparably lower crystallinity. In other words, the instant
polypropylene compositions and those of the prior art having crystalline

5   portions thereof at the same isotactic level have different heptane solubilities.
Accordingly, the catalyst system provides a polymerization process exhibiting
better control of undesirable amorphous (atactic) polymer, an unexpected result
over prior art processes employing other combinations of co-catalysts and
electron donors. These and other beneficial advantages will become more

10   apparent from the following detailed description of the invention and the
accompanying examples.

Electron donors are typically used in two ways in the formation of a
Ziegler-Natta catalyst component and a catalyst system. First, an internal

15   electron donor may be used as a stereoregulator in the formation reaction of the
catalyst as the transition metal halide is reacted with the metal hydride or metal
alkyl. The second use for an electron donor in a catalyst system is as an
external electron donor. It may exchange with the internal donor and change
the direction of stereoregulation of the catalyst system. The same compound

20   may be used in both instances, although typically they are different. Organic
silicon compounds, for example, dicyclopentyldimethoxysilane ("DCPMS"), are
common external electron donors. Examples of electron donors that are
organic silicon compounds are disclosed in U. S. Patent numbers 4,218,339;
4,395,360; 4,328,122; and 4,473,660, the entire disclosures of these patents

25   being hereby incorporated by reference for purposes of US patent practice. As
the present invention relates particularly to external electron donors, the term
"electron donor" as used herein, generally refers to the external donor unless
otherwise stipulated.

30   It has been discovered that the particular co-catalyst and electron donor
recipe of the present invention does significantly enhance the catalytic
properties of a solid titanium Ziegler-Natta catalyst component. The preferred
catalyst component demonstrating the most promising results in the present
invention is a new generation Ziegler-type titanium catalyst component for the

35   polymerization of olefins. This preferred catalyst comprises a solid catalyst
component obtained by (1) suspending a dialkoxy magnesium in an aromatic
hydrocarbon that is liquid at normal temperatures, (ii) contacting the dialkoxy

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magnesium with a titanium halide and further, (iii) contacting the resulting composition a second time with the titanium halide, and contacting the dialkoxy magnesium with a diester of an aromatic dicarboxylic acid at some point during the treatment with the titanium halide in (ii). A full description of these newer
5   generation catalyst components and their preparation are disclosed in the previously cited U. S. Patents owned by the Toho Titanium Company of Japan.

The present invention employs any magnesium-supported titanium-based catalyst components, such as the new generation Toho THC, or the more
10   conventional Ziegler-Natta components such as Mitsui TK-220, Himont FT4S, and HMC-101. Each can be combined with a mixture of organoaluminum co-catalysts, containing DEAC and a selected amount of an organosilane donor, such as MCMS or DCPMS to yield the catalyst system of this invention. The only constituent concentrations within the instant catalyst system that are
15   allowed to vary are (1) the ratio of DEAC to the other organoaluminum components in the co-catalyst mixture and (a) the amount of the organosilane external donor. It is the ratio of DEAC to the other organoaluminum components that establishes the low crystalline stereoregularity of the instant polypropylene compositions without the traditionally expected decreases in %
20   HI. As the relative amount of DEAC increases, the frequencies of stereo-defects increase in the crystalline component and consequently, the average *meso* run lengths become shorter. Structurally similar crystalline polypropylenes can be made with the use of conventional $TiCl_4$ supported catalyst system employing TEAl as the sole co-catalyst, but with considerably
25   higher levels of atactic polymer. By controlling the basic catalyst system recipe within the parameters of the present invention (such as the new generation Toho component catalyst with a specified amount of DEAC/TEAl co-catalyst and organosilane donor), it is possible to generate novel stereoregular polypropylenes of low crystallinity characterized by average *meso* run lengths of
30   less than 200 and lower than expected amounts of heptane solubles. For any other prior art catalyst recipe and choice of donor, polypropylene polymers of low crystallinity can be prepared only with unacceptable amounts of atactic polypropylene as reflected in relatively low heptane insolubles   (% HI).

35   While the ratios of (a) the catalyst component (b) the organoaluminum co-catalyst and (c) the silane electron donor components of the instant catalyst system are generally not critical one to the other,   (1) the relative amounts of

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DEAC to other organoaluminum co-catalysts and (2) the presence of
organosilane external donor are important to the practice of this invention.
Accordingly, the ratio of DEAC to the other organoaluminum compounds in
the co-catalyst mixture must be in an amount of from 3 to 75 mole percent, and

5   the organosilane electron donor is used in an amount of at least 0.1 part per
million (ppm) of total propylene in the reaction mixture.

        Preferred organoaluminum co-catalysts with the purview of the present
invention are alkylaluminum compounds such as trimethylaluminum,

10   triethylaluminum, tri-n-propylaluminum, tri-n-butyl-aluminum,
triisobutylaluminum, tri-n-hexylaluminum, trinormal-octylaluminum, and
diisobutylaluminum hydride. The most preferred alkylaluminum compound is
triethylaluminum.

15   Methods for determining the crystallinity of polypropylene include
measurements of the average *meso* run lengths ("MRL) and heats of fusion (Δ
H) of polypropylene. The heat of fusion is essentially a measurement of the
energy to melt the crystalline portion of a polypropylene composition and is a
direct measurement of crystallinity. The MRL is a structural measurement of

20   the average unperturbed lengths of the *meso* sequences in polypropylene chains,
which have the capability to crystallize in the polymer composition.

        A characterization curve of average *meso* run length versus heat of
fusion for traditionally prepared polypropylene and those polymers generated

25   with the catalyst system of the present invention is demonstrated in Figure 1.
The heat of fusion is determined by Differential Scanning Calorimetry ("DSC")
reflecting the crystallinity of the crystalline portion of the polymerized
propylene. The heat of fusion is a measure of the energy required to melt the
crystalline polypropylene sample and consequently is directly related to the level

30   of polypropylene crystallinity. The *meso* run length is the polypropylene
structural feature that is responsible for any observed crystallinity. Accordingly,
the curve illustrates higher crystallinity (heats of fusion) for those
polypropylenes with higher *meso* run lengths; that is, a direct relationship
between the physical measurement of crystallinity and the polymeric structural

35   reasons for expected crystallinity. Accordingly, the observed relationship
between the heats of fusion and average *meso* run lengths of Figure 1 allows the
meso run length also to be used as an indicator of incipient crystallinity of

polypropylene compositions of polypropylene prepared by prior art catalyst systems and the polypropylenes prepared by the catalyst system of the present invention.

5   The series of polypropylenes prepared by various traditional catalyst systems demonstrated in Figure 1 vary broadly in average *meso* (unperturbed) run lengths and, consequently, in the stereoregularity of the polypropylene polymers. As seen in Figure 1, the average *meso* run lengths, which are structural measurements, show a systematic relationship to the heats of fusion,

10   which are direct measures of polypropylene crystallinity. The average *meso* run lengths vary between 5 and 500 while the heats of fusion vary between 80 and 120 J/g. This range allows the relationship between the two different ways of evaluating polypropylene crystallinity to be fully observed. The plot clearly shows that the heat of fusion does not change significantly once the average

15   *meso* run length reaches values of 200 and higher. Below *meso* run lengths of 100, the heats of fusion respond dramatically to changes in the average *meso* run length. Atactic polypropylene typically has an average *meso* run length of around 5, whereas highly crystalline polypropylenes (heats of fusion above 105) have average *meso* run lengths in excess of 175 and beyond.

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           The crystallinity/stereoregularity plot of polypropylene compositions of Figure 1 is repeated in Figure 2 to demonstrate the relevant range of polypropylene compositions yielding low to moderate crystallinities. This is demonstrated by the bold lines defining the crystallinity regions of interest for

25   the polypropylene composition of the present invention. Numerically, this range of crystallinity occurs between average *meso* run lengths of 45 and 105, and heats of fusion between 75 and 109 J/g.

           The polypropylenes of the present invention have low to moderate

30   crystallinity, and have % HI's that do not follow the traditional relationship between HI and polypropylene crystallinity. In fact, they contain far less heptane soluble polypropylenes than would be ordinarily expected from their average level of crystallinity. To establish this characteristic of the present compositions, polypropylenes were prepared by the indicated catalysts to enable

35   the instant low to moderately crystalline polypropylene polymers to be compared to comparable, traditional polypropylenes (prepared with prior art

catalyst systems). The % heptane insolubles for the series of polypropylenes
were compared to both their respective heats of fusion and *meso* run lengths.

Tables I and II represent propylene polymerization test runs using the
catalyst system of the present invention which employs a new generation
catalyst component manufactured by the Toho Titanium Company of Japan and
commercially designated as the SP111 series. The characteristic curves of
Figures 3 - 6 represent the plotting of % HI, heats of fusion, and *meso* run
length values of Tables 1 and 2. The magnesium-supported Ziegler-Natta type
catalysts employed in the preparation of polymers for the test runs of Tables 1
and 2 are also listed along with the commercial polymer examined.

TABLE 1

LAB AND PILOT SCALE POLYMERIZATION WITH THE INVENTION CATALYST SYSTEM

Exp. No.	Scale	Cat. Component	MCMS Donor (ppm)	DEAC:TEAl (mole ratio)	Total Alkyls (ppm)	HI (%)	ΔH. (J/g)	MFR dg/min	Avg. meso run length
1	Lab	TOHO●	33	15:85	408	96.5	102	3.80	97
2	Lab	TOHO●	33	20:80	409	96.7	99	2.47	78
3	Lab	TOHO●	33	25:75	410	95.6	96	3.53	87
4	Pilot	TOHO●	32	15:85	70	98.8	109	2.80	188
5	Pilot	TOHO●	13	20:80	150	97.8	108	2.86	141
6	Pilot	TOHO●	13	25:75	400	95.6	98	2.50	94
7	Pilot	TOHO●	5	25:75	400	93.8	93	2.70	--
8	Pilot	TOHO●	1	25:75	400	90.5	90	2.60	65

CATALYSTS

TOHO●   ⇒   Mg-supported TiCl$_4$ catalyst commercially available from TOHO Titanium Co. of Japan

TABLE 2

Exp. No.	Scale	Cat.	MCMS Donor (ppm)	DEAC:TEAl (mole ratio)	Total Alkyls (ppm)	HI (%)	ΔH (J/g)	MFR dg/min	Avg. *meso* run length
9	Lab	TOHO•	0	25:75	400	88.2	87	12.8	--
10	Lab	TOHO•	0	0:100	400	91.0	93	2.31	76
11	Lab	TK-220◆	0	0:100	400	82.9	80	3.03	57
12	Pilot	TOHO•	0	0:100	70	90.2	93	2.80	86/94
13	Pilot	TOHO•	1	0:100	70	97.2	104	2.80	96
14	Lab	HMC-101✚	0	0:100	400	84.3	83	6.04	69
15	Pilot	TiCl₃*	20 (MMA)	100:0	500	95.0	106	2.90	--
16	Comm.	Fina 3378⊗	Polymer	--		93.7	101	2.80	109

CATALYSTS

TOHO•   ⟹   Mg-supported $TiCl_4$ catalyst commercially available from TOHO Titanium Co. of Japan

TK220◆   ⟹   Mg-supported $TiCl_4$ catalyst available from Mitsui Corporation

HMC-101✚   ⟹   Mg-supported $TiCl_4$ catalyst available from HIMONT Corporation

TiCl₃*   ⟹   High-Activity $TiCl_3$ catalyst based on US Patent 4,295,991

FINA 3378⊗   ⟹   Commercial polymer made by Fina Technology, Inc., Dallas, Texas

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The experimental data in Tables 1 and 2 were generated as follows:

EXPERIMENTAL

(A)   DSC (Differential Scanning Calorimetry)

A TA-200/DSC-10 instrument, purchased from TA Instruments, Inc., was used to measure the thermal properties of the polymers. The polymers were first extruded and pelletized prior to taking a 8-13 mgs samples. A prepared DSC sample was placed in the cell and the cell purged with nitrogen at room temperature for five minutes. The temperature was then raised to 230°C at a heating rate of 50°C per minute. The temperature was held for ten minutes, followed by cooling to 50°C at a cooling rate of 10°C per minute. After reaching 50°C, the sample was again heated to 200°C at the rate of 10°C per minute. The heat of melting during the second heating cycle was measured, by integrating the melting curve between baseline limits of 85 and 175°C, and used to determine relative crystallinities of the indicated polypropylenes.

(B)   Polymerization Process in a Batch Reactor

An amount of silane donor (in a 0.01M solution in hexane as parts per million donor by weight relative to the total amount of propylene employed) was charged by syringe into a 2 liter autoclave polymerization reactor that had been thoroughly cleaned, dried, and purged with nitrogen. A specified total amount of aluminum alkyl (as parts per million by weight at the desired molar mixture of DEAC and TEAl) was then added to the reactor. A desired amount of hydrogen was introduced into the reactor, as measured by the psi drop from a 300 cc vessel. Next, 1000 ml of propylene was added to the reactor. These procedures were followed by introducing the required amount of catalyst (at 15 to 20 weight percent solids in a mineral oil slurry) by pushing the catalyst into the reactor with 250 cc of propylene. The reactor temperature was raised form room temperature to 70°C and the reaction was allowed to continue for one hour. After the polymerization period, the excess propylene was vented out of the reactor and the remaining polymer was collected and dried in a vacuum oven. The polymer was pelletized with the addition of 500 ppm BHT and samples were taken for % HI, MFR, DSC (ΔH) and NMR measurements.

(C)   Polymerization Process in a Continuous Pilot Plant Reactor

Continuous polymerizations were carried out using a series of two autoclave reactors which are capable of producing 90 pounds of polymer per hour. The conditions were similar to those of (B), with the exception that the catalyst, silane donor, and mixed DEAC/TEAl reagents were added continuously, and polymerizations were conducted for 4 to 4.5 hours. The subsequent polymers were pelletized prior to taking samples and making the required measurements.

(D)   Characterization

Turning to Figures 3 and 4, two views of a plot of % HI versus heat of fusion can be found for both the compositions of the invention and traditional polypropylenes over a broad range of crystallinity. The "window" area, described as "10" in Figure 3, represents that area of low to moderate crystallinity, which characterize the instant polypropylene compositions. This area is equivalent to the defined area of crystallinity demonstrated in Figure 2. Figure 3, which gives a complete view of the relationship between % heptane insolubles and heats of fusion as an index of crystallinity, contains data points generated from compositions ranging from atactic polypropylene with no low crystallinity to highly crystalline polypropylenes. It is clear in Figure 3 that the % heptane insolubles and heats of fusion demonstrate a proportionally linear relationship with curvature developing only at the higher values for the heats of fusion   (Δ H) and % HI. Also shown in Figure 3 is a calculated line, described as "11", which defines the boundary between polypropylenes generated by the traditional catalyst systems and those polypropylenes generated by the instant catalyst system.

Figure 4 is an expanded view of the window area 10 in Figure 3 demonstrating two calculated lines, 11 and 12. Upper calculated line 11 corresponds to the same calculated line 11 shown in Figure 3. The position of the lower line 12 in Figure 4 was determined after a linear regression analysis over the ΔH, HI relationship for the series of polypropylenes, described as

"traditional" i.e., prepared from traditional catalyst systems of the prior art. The algebraic equation for line 12 is as follows:

$$\% \text{ HI Limit} = 0.477(\Delta H) + 44.6 \qquad (1)$$

Note that the "traditional polypropylenes" have relatively low % heptane insolubles compared to those defined as "new generation" and "invention polypropylenes". To define the relationship observed with the "new generation" catalyst recipe of the present invention, the second and higher line 11 is shown in Figure 4. It is the same line shown in Figure 3. The algebraic equation for line 11 was also determined through linear regression analysis and is given by:

$$\% \text{ HI Limit} = 0.545 (\Delta H) + 40.50 \qquad (2)$$

This line provides a boundary between those regions defining the polypropylenes prepared with prior art catalyst systems and those polypropylene compositions prepared with the instant catalyst system. Note that the invention polypropylenes have the highest observed % HI in the ΔH range from 85 to 100 J/g. Any catalyst generated polypropylene composition having atactic polymer content and crystallinity values that give a point above line 11 falls within the purview of the instant invention, which is directed toward low to moderately crystalline polypropylenes having relatively high HI's. Note from Tables 1 and 2 that traditional polypropylene of run # 12 and invention polypropylene of run # 7 have similar heats of fusion, that is, 92.6 and 92.5 J/g, respectively. The % HI for # 12 is 90.2, which places the composition below the line, and the % HI for composition # 7 is 93.8, which places it above the line. Six of the eight polypropylenes prepared with the instant catalyst system place above the indicated line. The other two, which incidentally place just below line 11, fall outside the defined region of compositions characterized in the present invention (their heats of fusion are close to 109 J/g).

It should also be noted that % HI versus ΔH relationship is treated as linear, when actually it is nonlinear. This means that the linear relationship is further from the actual relationship at heats of fusion values greater than 100 J/g and below 90 J/g. The deviations of the traditional relationship from the straight line, defined by Equation 2, can easily be seen in Figure 3. Treating the % HI vs.

ΔH invention boundary as linear, as opposed to nonlinear, in the regions outlined by the window 10 in Figures 3, which is amplified as Figure 4, is a more conservative approach for characterizing the instant compositions than using a nonlinear relationship between HI and ΔH because the "ends" of the line are further from the actual relationship than the "center" of the line. This restricts the region defining the instant compositions even more than was empirically obtained when plotting actual values of HI and ΔH.

Figures 5 and 6 are different views of the % HI versus average *meso* run length relationship for both prior art and invention polypropylenes. (The procedure for producing Figures 5 and 6 is comparable to the procedure for producing Figures 4 and 5.) Figure 5 shows the full relationship from atactic polypropylene to highly crystalline polypropylenes while Figure 6 is an expansion of the outlined window area 20 in Figure 5. Analogous to the procedure employed in Figure 4, calculated line "13" line is used in Figure 5 to define the boundary between traditional polypropylenes and those of the polymers prepared with the catalyst system of the present invention. A lower calculated line, "14" is also given in the expanded view of the % HI versus *meso* run length relationship shown in Figure 6, analogous to the linear relationships shown in Figure 4. Line 14, which defines the "traditional" polypropylene relationship was determined by performing a linear regression analysis over the traditional prior art polypropylenes. The algebraic equation for line 14 is given below:

$$\% \text{ HI Limit} = 0.117 \text{ (MRL)} + 76.2 \qquad (3)$$

Note that the traditional polypropylenes give the lowest % HI at *meso* run lengths between 55 and 95.

The second and higher line 13, shown in Figure 6, is the relationship observed for the polypropylenes prepared with the commercial Toho catalyst recipe. The equation for this line, which was also shown in Figure 5, defines the boundary between the invention and traditional polypropylenes and is given below:

$$\% \text{ HI Limit} = 0.31 \text{(MRL)} + 67.4 \qquad (4)$$

As observed in the relationship between ΔH and % HI, the invention catalyst recipes give polypropylenes that have higher % HI's than the traditional polypropylenes. Both equations 2 and 4 describe boundaries between similar ranges of crystallinity. The HI limits of 81.3 and 100 were used to establish the MRL range of 45 to 105 and the ΔH range of 75 to 109 J/g.

Three of the five polypropylenes within the purview of the instant invention fall in the region above the upper straight line in Figure 6. Two are close to, but below, the boundary as a consequence of the fact that the actual relationship is nonlinear and these points fall in the region where the line that defines the boundary between invention and traditional polypropylenes is furthest from the actual relationship. The presence of a traditional data point in this region is another reason to use the linear relationship as the invention and traditional polypropylenes data also begin to merge at ΔH's above 108-110 J/g and *meso* run lengths above 95-100. Although some invention compositions, particularly for *meso* run lengths over 90, will be excluded from the purview of · this invention, optimum compositions in this range will still fall above the line. Most traditional compositions fall well below the line as shown by the data in Figure 6.

The polypropylenes, which fall clearly and distinctively within the purview of the present invention will be identified by the combined measurements of average *meso* run length and % HI. Equations 2 and 4, given above, when used in the range of crystallinity defined by average *meso* run lengths between 45 and 105 and corresponding heats of fusion, between 75 and 109 J/g define the moderate to low crystalline polypropylene compositions of the present invention.

Experimentally measured heats of fusion, *meso* run lengths and % HI are compared to the calculated % HI limits, defined by Equations (2) and (4) in the following Table 3. Negative deviations from the calculated HI limits are compositions falling within the purview of the present invention. This is indicated by either Δ1 or Δ2, as given below:

$$\Delta1 = \text{Calculated \% HI Limit (Eqn. 4) - Exp. \% HI} \qquad (5)$$
$$\Delta2 = \text{Calculated \% HI Limit (Eqn. 2) - Exp. \% HI} \qquad (6)$$

TABLE 3

Experimentally measured % HI versus
those calculated from equations (1) and (2) using experimentally
determined *meso* run lengths and heats of fusion.

Sample	MRL	Heat of Fusion			% Heptane	Insolubles	
			Exp.	Eqn. 1	Eqn. 2	Δ1	Δ2
1	97	101.6	96.5	95.8	97.5	1	-0.7
2	78	98.6	96.7	94.2	91.6	-5.1	-2.5
3	87	96.2	95.6	92.9	94.4	-1.2	-2.7
6	94	97.8	95.6	93.8	96.6	1	-1.8
8	65	89.5	90.5	89.3	87.6	-2.9	-1.2
13	96	103.6	97.2	96.9	97.2	0	-0.3
10	76	93.2	91	91.3	91	0	0.3
12	94	92.6	90	90.9	96.6	6.6	0.9
12	86	92.6	90	90.9	94.1	4.1	0.9
11	57	80	82.9	84.1	85.1	2.2	1.2
14	69	83.3	84.3	85.9	88.8	4.5	1.6
Test 1	105	109		100	100		
Test 2	45	75		81.3	81.4		

$$\% \text{ HI} = 0.545 \ (\Delta \text{ H}) + 40.5 \qquad (1)$$
$$\% \text{ HI} = 0.31 \ (\text{MRL}) + 67.4 \qquad (2)$$
$$\Delta 1 = \text{Calculated } \% \text{ HI Limit (Eqn. 2)} - \text{Exp. } \% \text{ HI} \qquad (3)$$
$$\Delta 2 = \text{Calculated } \% \text{ HI Limit (Eqn. 1)} - \text{Exp. } \% \text{ HI} \qquad (4)$$

(E) Electron Donors

The electron donors included in the present invention are organic silicon compounds such as those described above in the prior art. Typical organosilane compounds used as external donors in the catalyst system of the present invention include those disclosed in U. S. Patent 4,990,479 to Ishimaru et al. the entire disclosure of which is hereby incorporated by reference for purposes of US patent practice. Preferred organosilane electron donors include methylcyclohexyldimethoxysilane ("MCMS"), dicyclopentyldimethoxy-silane ("DCPMS"), diphenyldimethoxysilane ("DPMS"). The most preferred electron donor is methylcyclohexyldimethoxysilane ("MCMS"). The combination of MCMS and the catalyst/co-catalyst subsystem described herein yields wholly unexpected results that surpass previously known catalyst systems. The electron donors as described for use in the present invention may be limited by the stability of the compound and the ease of handling including storage, transportation, and use in the plant.

(F) Prepolymerization

The present invention also provides a process for the polymerization of olefins using the catalyst system described above. Although the catalyst system may be used in almost any commercially known polymerization process, the preferred process of the present invention includes a pre-polymerization of the catalyst with a small amount of monomer as described in numerous prior art patents. For example a carrier stream for the catalyst is provided, the catalyst is contacted with the co-catalyst organoaluminum compound mixture and subsequently contacted with the electron donor. The catalyst stream is then contacted with a relatively small amount of the total amount of monomer to be polymerized, the catalyst stream passing through a tubular or stirred reactor, and the pre-polymerized catalyst and catalyst stream are introduced into the polymerization reaction zone. The electron donor may be contacted with the catalyst simultaneously with the co-catalyst mixture. A polymer product may then be withdrawn from the reactor. In using the described catalyst component with the co-catalyst mixture and electron donors described above, the catalyst system may have an efficiency of at least about 20 kg/gcat. while the Al/Si mole

ratio in the reaction is within the range 5-1000. The polymer product will also be characterized by hexane solubles within the range 2-10 weight percent.

Having described several specific embodiments of the present invention, it will be understood by those skilled in the art that modifications may be made without departing from the scope of the present invention.

We claim:

1.   An olefin polymerization catalyst system comprising:

        (i)   a solid titanium catalyst component including magnesium,
                 titanium, halogen, and an internal electron donor;

        (ii)   a co-catalyst mixture of at least two organoaluminum halide
                 compounds including a first organoaluminum halide,
                 diethylaluminum chloride in a quantity of between 3 to 75 mole
                 percent of the total organoaluminum co-catalyst mixture and a
                 second organoaluminum halide being one of trimethylaluminum,
                 triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum,
                 triisobutylaluminum, tri-n-hexylaluminum,
                 trinormaloctylaluminum, diisobutylaluminum hydride and mixtures
                 thereof, preferably triethylaluninum; and

        (iii)   an external organosilane electron donor.

2.   The catalyst system of claim 1 wherein the organosilane is selected from
        the group consisting of methylcyclohexyldimethoxysilane,
        dicyclopentyldimethoxysilane, diphenyldimethoxysilane, phenyl-
        triethoxysilane, and propyltriexthoxysilane, preferably
        methylcyclohexyldimethoxysilane or dicyclopentyldimethoxysilane.

3.   An olefin polymerization catalyst system comprising:

        (i)   a solid catalyst component prepared by (i) suspending a dialkoxy
                 magnesium in an aromatic hydrocarbon that is liquid at normal
                 temperatures, (ii) contacting the dialkoxy magnesium with a
                 titanium halide and further contacting the resulting composition a
                 second time with the titanium halide and (iii) contacting the
                 dialkoxy magnesium with a diester of an aromatic dicarboxylic
                 acid at some point during the treatment with the titanium halide in
                 (ii); and

(ii)   a co-catalyst mixture including of at least two organoaluminum halide compounds including a first organoaluminum halide, diethylaluminum chloride, present in the mixture in a quantity of between 3 to 75 mole percent of the total organoaluminum co-catalyst and a second organoaluminum halide being one of trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-n-hexylaluminum, trinormaloctylaluminun, diisobutylaluminum hydride, and mixtures thereof, preferably triethylaluminum; and

(iii)   an external organosilane electron donor.

4.   The olefin polymerization catalyst system of claim 3 wherein the organosilane is selected from the group consisting of methylcyclohexyldimethoxysilane, dicyclopentyldimethoxysilane, diphenyldimethoxysilane, phenyltriethoxysilane, and propyl-triexthoxysilane preferably methylcyclohexyldimethoxysilane or dicyclopentyldimethoxysilane.

5.   The use of the catalyst systems of claims 1 or 3 in a process for the polymerization of olefins including:

(a)   providing the catalyst system of claims 1 or 3; and

(b)   introducing the catalyst system into a polymerization reaction zone containing additional amounts of the organoaluminum halide co-catalyst mixture, the organosilane electron donor, and an olefin monomer wherein polymerization of the monomer takes place to form a polyolefin.

6.   The process of claim 5 further including the step of prepolymerizing the catalyst system before introduction to the reaction zone by contacting a small amount of olefin monomer with the catalyst system.

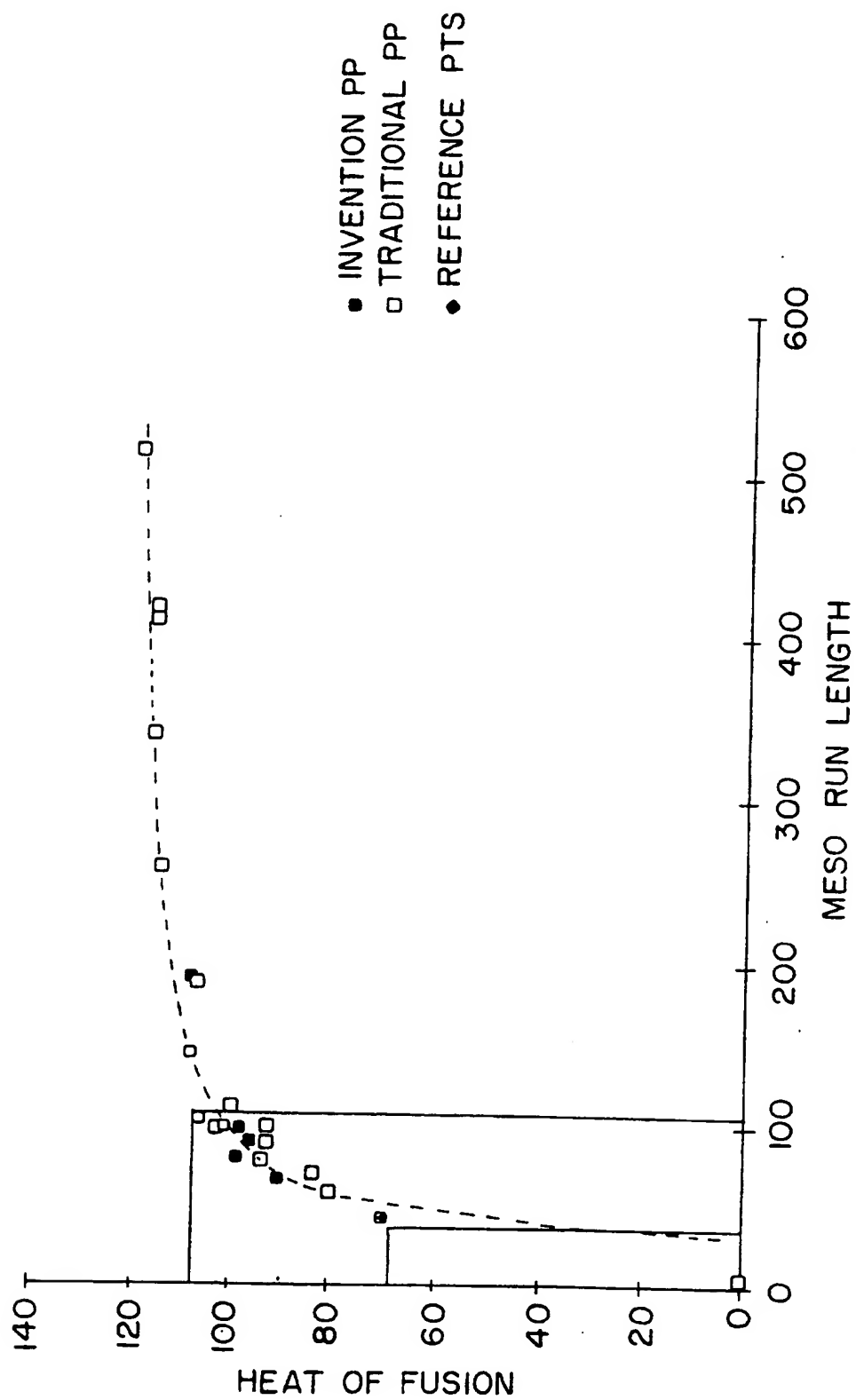7.   The process of claim 5, further comprising the additional step of:

(c)   removing the polyolefin polymer from the reaction zone.

8.   The process of claim 7 wherein the removed polyolefin is characterized by average *meso* run lengths of between 45 and 105, a heat of fusion between 81.3 and 109, and heptane insolubility values falling above either line, represented by the algebraic equations:

$$\% \text{ HI} = 0.545\ (\Delta\text{H}) + 40.5 \text{ or } \% \text{ HI} = 0.31\ (\text{MRL}) + 67.4.$$
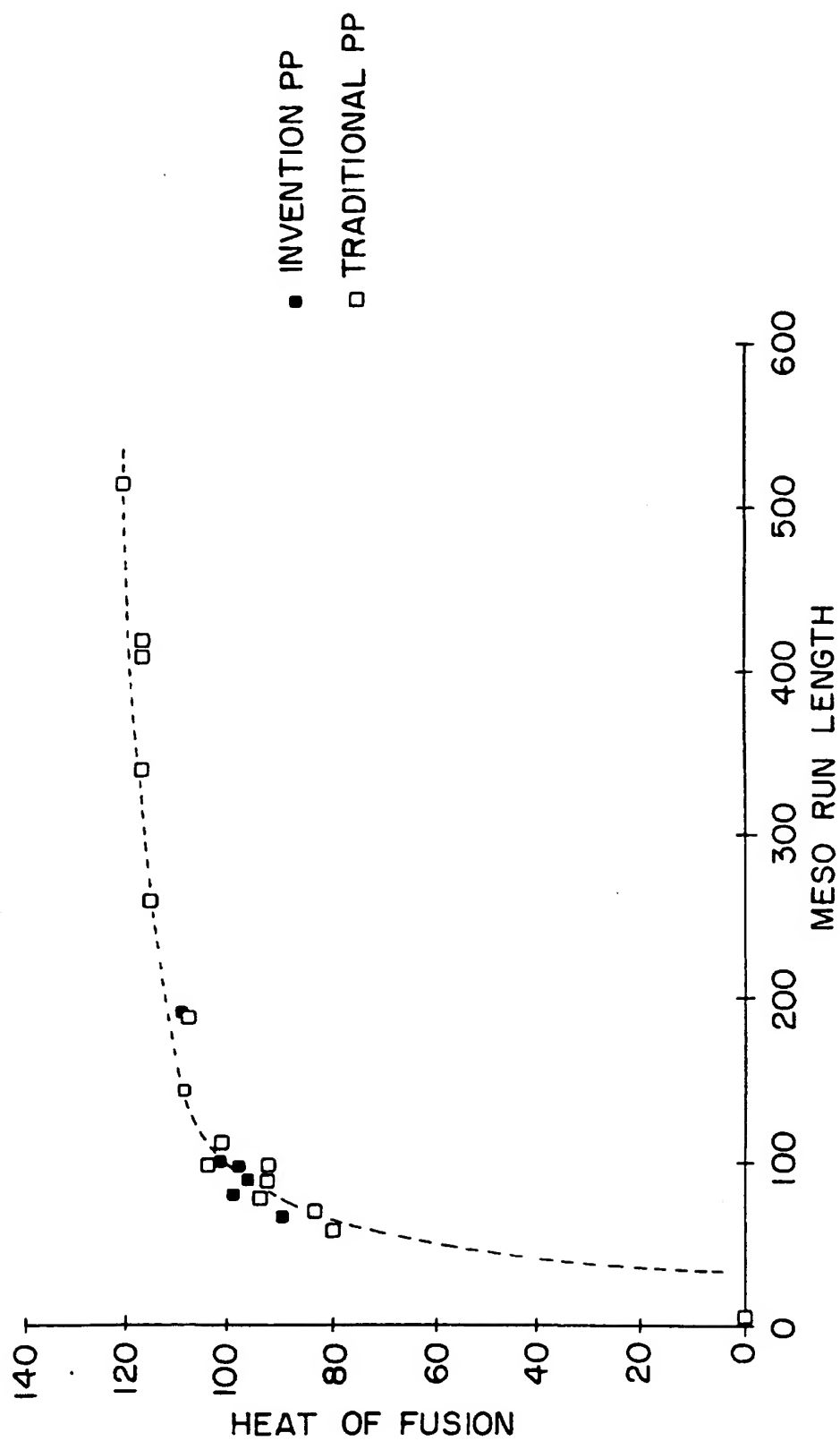
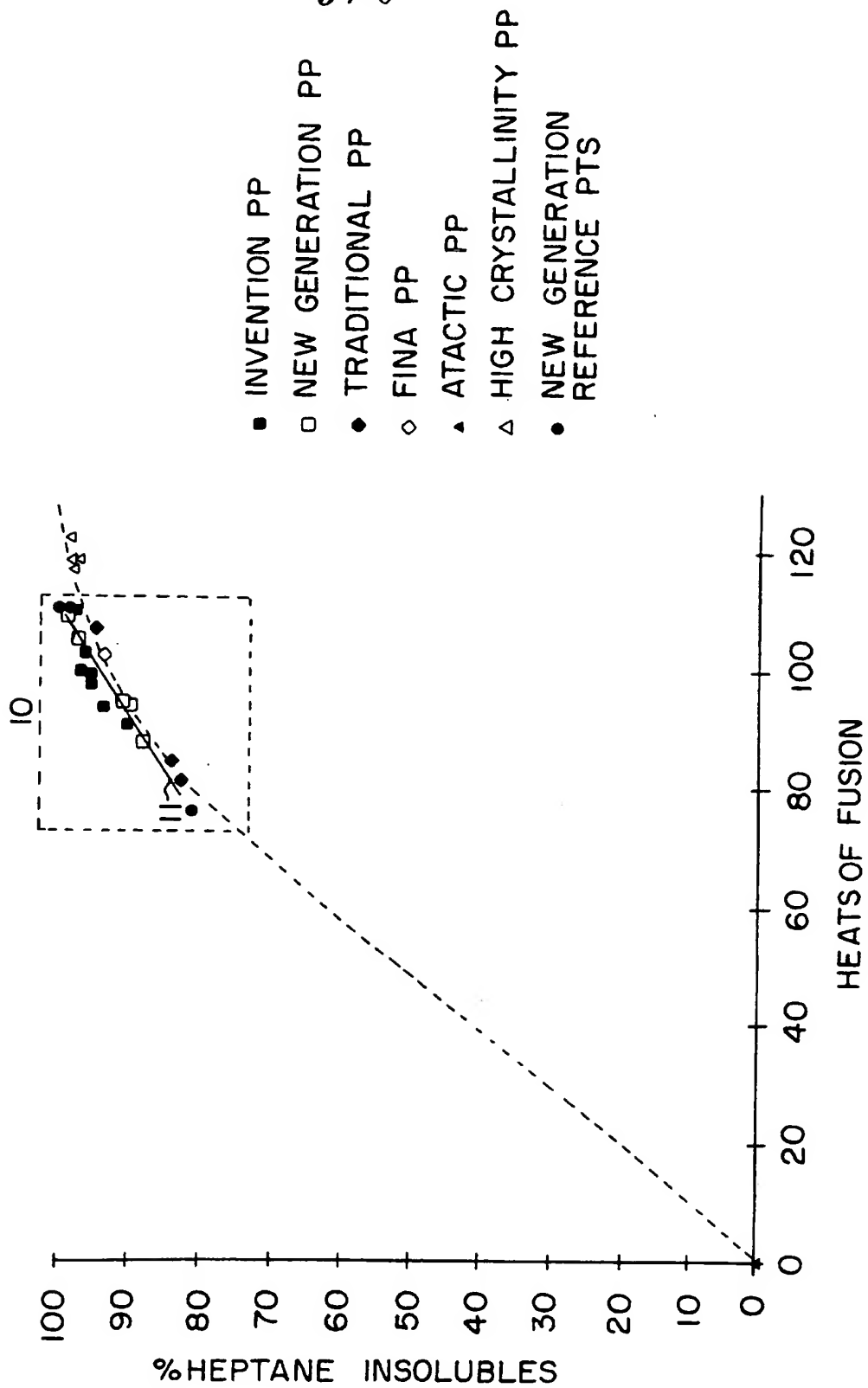9.   The polyolefin prepared by the process of claim 5.

10.   A polypropylene polymer composition characterized by having an average *meso* run length between 45 and 105, a heat of fusion between 81.3 and 109, and a heptane insolubility falling above either line, represented by the algebraic equations:

$$\% \text{ HI} = 0.545\ (\Delta\text{H}) + 40.5 \text{ or } \% \text{ HI} = 0.31\ (\text{MRL}) + 67.4.$$

AMENDED CLAIMS

[received by the International Bureau on 23 January 1996 (23.01.96);
Original claim 10 cancelled; remaining claims unchanged (1 page)]

(c)   removing the polyolefin polymer from the reaction zone.

8.   The process of claim 7 wherein the removed polyolefin is characterized by
average *meso* run lengths of between 45 and 105, a heat of fusion
between 81.3 and 109, and heptane insolubility values falling above either
line, represented by the algebraic equations:

$$\% \, HI = 0.545 \, (\Delta H) + 40.5 \text{ or } \% \, HI = 0.31 \, (MRL) + 67.4.$$

9.   The polyolefin prepared by the process of claim 5.

AMENDED SHEET (ARTICLE 19)

FIG.2

MESO RUN LENGTH

HEAT OF FUSION

- INVENTION PP
□ TRADITIONAL PP
♦ REFERENCE PTS

FIG.1

FIG. 3

- ■ INVENTION PP
- □ NEW GENERATION PP
- ♦ TRADITIONAL PP
- ◇ FINA PP
- ▲ ATACTIC PP
- △ HIGH CRYSTALLINITY PP
- ● NEW GENERATION REFERENCE PTS

FIG. 4

% HEPTANE INSOLUBLES vs **HEATS OF FUSION**

Legend:
- ■ INVENTION PP
- □ NEW GENERATION PP
- ◆ TRADITIONAL PP
- ◇ FINA PP
- ▲ ATACTIC PP
- △ HIGH CRYSTALLINITY PP
- • NEW GENERATION REFERENCE PTS
- ○ TRADITIONAL REFERENCE PTS

FIG.5

FIG.6

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C08F10/00   C08F4/646

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 584 586 (HOECHST AKTIENGESELLSCHAFT) 2 March 1994 see claims 1-4	1,2
Y	see example 1	3-5,7,9

Y	EP,A,0 565 173 (TOHO TITANIUM CO LTD) 13 October 1993 see claims 1,5 see example 1	3-5,7,9

P,X	POLYMER BULLETIN, vol.35, no.1-2, , BERLIN pages 115 - 120, XP000507168 see page 116, paragraph 2 -paragraph 3 see column 5; table 1 see page 119, paragraph 2	1,2

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 October 1995	29.12.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	FISCHER B.R.

4

INTERNATIONAL SEARCH REPORT

Internatic   application No.

PCT/US95/09670

Box I   Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II   Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

> 1. Claims 1-9: Catalyst system, process using it andproduct obtained therewith
>
> 2. Claim   10: Polypropylene composition as such

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searches without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest   ☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1992)

INTERNATIONAL SEARCH REPORT

Info. ...ion on patent family members

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0584586	02-03-94	AU-B-	4446093	10-02-94
		CA-A-	2103694	09-02-94
		CZ-A-	9301605	16-03-94
		JP-A-	6157664	07-06-94
EP-A-0565173	13-10-93	JP-A-	6166716	14-06-94
		JP-A-	5301918	16-11-93
		JP-A-	6166717	14-06-94

Microtacticity Distribution of Polypropylenes Prepared with Heterogeneous Ziegler–Natta Catalysts

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ABSTRACT: The microstructure of the isotactic parts of various polypropylenes has been studied by ^{13}C NMR spectroscopy. The isotacticity of the isotactic parts as determined by the $mmmm$ pentad sequence ("microisotacticity") increases as the stereospecificity of the catalysts (isotactic index, II) employed increases. Several polypropylenes prepared with titanium-based catalysts were fractionated by using an elution column technique. The fractionation results show that two isospecific active centers reside in such catalysts. The proportion of those active centers varies with catalyst; the highly isospecific center increases with the stereospecificity (II). This fact accounts for the above relationship between the microisotacticity and the stereospecificity. On the basis of these results, new models for the active centers are proposed.

Introduction

It is well-known that heterogeneous Ziegler–Natta catalysts yield a mixture of polypropylenes having different stereoregularities, i.e., isotactic and atactic. From the industrial point of view, the formation of atactic polymer is a key concern because it has a great influence on the production cost and the physical properties of the products. Thus, efforts have been directed toward the reduction of atactic polymer. On the other hand, it is the isotactic polymer that is the major component of commercial polypropylenes. For example, the isotactic index (II) of commercial polypropylenes (i.e., boiling heptane insoluble fraction) generally exceeds 95%. Therefore, the molecular microstructure of an isotactic polymer probably has a significant influence on the properties of the products. Although the microtacticity of the isotactic parts is known to vary subtly with catalyst system,[1-5] no detailed studies have so far been carried out. The objective of the present paper is specifically to understand the relationship between the nature of catalysts and the molecular structure of the isotactic parts. First, the isotactic fractions of polypropylenes polymerized with a wide range of heterogeneous catalysts have been examined by ^{13}C NMR spectroscopy. Next, a microtacticity distribution of several polypropylenes has been determined by temperature-programmed column fractionation. As a result, it has been found that: (1) two isospecific active centers are present and (2) the relative proportion of the active centers varies with catalyst. These results will be discussed on the basis of the newly proposed models for the active centers.

Experimental Section

Catalysts. δ-TiCl$_3$HA, δ-TiCl$_3$AA, δ-TiCl$_3$ (Solvay), CrCl$_3$, and VCl$_3$ were purchased and were used without any treatment except that CrCl$_3$ was ball-milled for the purpose of improvement of its catalytic activity. δ-TiCl$_3$HA was obtained from Toyo Stauffer Chemical and had been prepared by reduction of TiCl$_4$ with hydrogen, followed by ball-milling. δ-TiCl$_3$AA which had been prepared by reduction of TiCl$_4$ with aluminum followed by ball-milling for activation was also obtained from Toyo Stauffer Chemical. δ-TiCl$_3$ (Solvay) was obtained from Solvay-Marubeni Chemicals Co. β-TiCl$_3$ was prepared from the Natta complex according to Smith and Perry.[6] MgCl$_2$-supported Ti catalyst was prepared according to the Sumitomo Chemical Co. patent.[7] Ethylaluminum (EtAl) cocatalysts and methyl p-toluate as an electron donor were purchased and were used without any purification.

Polymerization. Polymerization was carried out in a 5-L autoclave in liquefied propylene or in n-heptane, both of which were dried on a molecular sieve 13X in advance. The polymerization was terminated by adding isobutyl alcohol. After the catalyst residues were removed with a mixture of 1 N HCl and

methanol (1/1 v/v), the product was dried in vacuo at 50 °C for 4 h. Detailed polymerization conditions are given in Tables I and II. The aging of δ-TiCl$_3$AA was carried out at 70 °C similarly to the polymerization except that there was no feed of the monomer; after 3.5 h the polymerization was initiated by introducing the monomer.

Solvent Extraction. The sample was completely dissolved in boiling xylene and then the solution was cooled gradually to 20 °C. The precipitated polymer was separated from the solution by filtration. The polymer soluble in xylene at 20 °C was recovered from the filtrate by evaporation. Further, the precipitated polymer was extracted with boiling n-heptane in a Soxhlet extractor.

Elution Column Fractionation. Ten grams of the whole polymer was dissolved at 130 °C in xylene, and then 1200 g of sea sand (35–48 mesh) kept at 130 °C was put into the solution. The mixture was cooled gradually to 20 °C. Through this treatment, the higher isotactic polymer will be deposited first and the lower last, which will achieve a satisfactory fractionation. Then the mixture was put into a column (74 mm in diameter and 435 mm in height) immersed in an oil bath maintained at 20 °C. The first fractionation was eluted at 20 °C by dropping xylene into the column. Five hundred milliliters of xylene was used to elute each fraction. However, when a precipitate or milky turbidity appeared by addition of last several droplets of the eluate into methanol, some additional xylene was introduced until it did not appear. The time taken was about 1 h. The consecutive fractions were obtained by raising the elution temperature stepwise up to 130 °C. The polymer fractions were precipitated by addition of the eluates by into 2.5 L of methanol, recovered by filtration, and dried in vacuo. The fractions were obtained every 10 to 20 °C in the region 20–60 °C, every 2 to 10 °C in the region 60–90 °C, every 1 to 2 °C in the region 90–110 °C, and every 0.5 to 1 °C at over 110 °C. The elution temperature was controlled within ±0.1 °C. As a result, the number of the fractions varies from 16 to 38, depending on the isotacticity of the samples. The differential distribution was determined from slope of the cumulative distribution.

^{13}**C NMR Measurement.** ^{13}C NMR spectrum was obtained at 135 °C on a JEOL FX-100 pulsed Fourier transform NMR spectrometer. Experimental procedure and instrument conditions are described in a previous paper.[8] Pentad tacticity was determined from the area of the resonance peaks of the methyl region. Pentad sequences are represented by a sequence of m = meso (isotactic diads) and r = racemic (syndiotactic diads).

Melting Temperature Measurement. The melting temperature of the sample was measured on a Perkin-Elmer type-differential scanning calorimeter (DSC). The sample was premelted in DSC at 220 °C for 5 min and was rapidly cooled to room temperature. The thermogram was recorded by raising the temperature from 40 to 180 °C at a rate of 5 °C/min.

Results

Extraction of Polypropylenes Polymerized with Various Catalyst Systems. A variety of polypropylenes prepared with transition-metal halides such as TiCl$_3$, VCl

Table I
Stereoregularity of Polypropylenes Prepared with Various Catalysts Systems

| sample | catalyst system | polymerization[a] | | | solvent extraction | | microisotacticity[d] |
		temp, °C	time, h	catal act, g of PP/(g of cat h)	atactic,[b] %	isotactic,[c] %	
1	δ-TiCl₃AA–AlEt₂Cl	60	1	400	5.00	90.2	0.967
2	δ-TiCl₃Sol[e]–AlEt₂Cl	60	1	2000	3.0	92.2	0.973
3	δ-TiCl₃HA–AlEt₂Cl	65	4	120	10.7	82.9	0.962
4	β-TiCl₃–AlEt₂Cl	65	4	140	62.6	18.7	0.956
5	VCl₃–AlEt₂Cl	65	4	50	55.1	14.3	0.956
6	CrCl₃–AlEt₂Cl	65	4	1	18.4	71.7	0.960
7	δ-TiCl₃AA–AlEt₃	60	1	710	14.9	60.0	0.964
8	δ-TiCl₃AA–AlEt₂Br	60	1	530	6.0	88.4	0.965
9	δ-TiCl₃AA–AlEt₂I	60	1	200	2.9	92.9	0.975
10	δ-TiCl₃SOL–AlEt₃	70	1	5600	23.3	59.1	0.958
11	δ-TiCl₃SOL–AlEt₂I	50	1	600	1.0	95.4	0.983

[a] Other polymerization conditions: 5-L autoclave; propylene, 33 mol; H₂, 2–5 vol %; AlEt₂Cl, 25 mmol; AlEt₃, 4 mmol; AlEt₂Br, 25 mmol; AlEt₂I, 25 mmol. [b] % fraction soluble in xylene at 20 °C. [c] % fraction insoluble in boiling n-heptane. [d] [mmmm] fraction of the fraction insoluble in boiling n-heptane. [e] δ-TiCl₃ (Solvay).

Table II
Sample List for Fractionation

| sample | catalyst system | polymerization[a] | | | | IV,[b] dL/g | solvent extraction | | microisotacticity |
		time, h	pressure, kg/(cm G)	H₂, vol %	catal act, g of PP/(g of cat h)		atactic,[c] %	isotactic,[c] %	
12	β-TiCl₃–AlEt₂Cl	0.5	10	1.5	80	0.6	62.7		0.955
13	δ-TiCl₃AA–AlEt₂Cl	0.5	10	5.1	640	1.6	5.1		0.967
14	δ-TiCl₃AA–AlEt₂Cl	0.5[d]	10	3.7	420	1.5	6.2		0.964
15	Mg–Ti(I)[e]–AlEt₃	1.0	6	2.8	8900	0.7	43.0	28.0	0.954
16	Mg–Ti(I)[e]–AlEt₃–MT[f]	1.0	6	2.8	5400	1.8	4.7	88.4	0.970

[a] Other polymerization conditions: 5-L autoclave; solvent n-heptane, 1.5 L; polymerization temperature, 70 sC; AlEt₂Cl 12.5 mmol; AlEt₃, 4.0 mmol; MT, 0.88 mmol. [b] Intrinsic viscosity. [c] See Table I. [d] The catalyst was aged for 3.5 h at 70 °C in advance of polymerization. [e] According to U.S. Patent 4 223 117 (Sumitomo Chemical Co.). [f] Methyl p-toluate.

and CrCl₃ and MgCl₂-supported Ti catalysts with and without methyl p-toluate as an electron donor were divided into three fractions, those soluble in xylene at 20 °C, soluble in boiling heptane, and insoluble in boiling heptane, by conventional solvent extraction method. The stereoregularity of the fractions insoluble in boiling heptane was determined by ¹³C NMR spectroscopy. The extraction data are shown in Tables I and II. As seen from these tables, the percent of atactic polymer (soluble in xylene at 20 °C) varies over a wide range of 1–63% and at the same time the II ranges from 14 to 95%. In addition, the isotactic (mmmm) pentad fraction of the isotactic parts as measured by ¹³C NMR also varies ranging from 0.956 to 0.983. The isotactic pentad fraction will hereinafter be termed "microisotacticity" in order to be distinguished from the so-called isotactic index, II. Similarly the ability to regulate the microisotacticity will be termed "microisospecificity".

Strangely, the data shown in Tables I and II suggest that the variation of microisotacticity may have some relation to that of percent atactic polymer. As noted in Figure 1, the microisotacticity shows a tendency to decrease with increasing percent atactic polymer. Although a MgCl₂-supported Ti catalyst is not highly stereospecific in the absence of an electron donor, it is of interest that the microisotacticity also decreases in its absence. The pentad stereoirregularities found in all the isotactic parts are only mmmr, mmrr, and mrrm. The ratio of those intensities is approximately 2:2:1. This fact indicates that isotactic propagation on all the catalysts used here is governed by catalytic control,[1,10] which means that the nature of the isotactic active center determines the microisotacticity. On the other hand, the percent atactic polymer is presumed to reflect only the relative concentration of the atactic active center. Therefore, it is rather unusual that the microisospecificty of the isotactic active center is directly
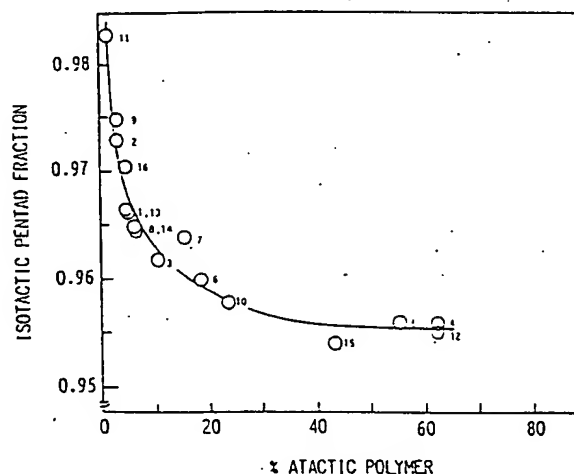

Figure 1. Plot of microisotacticity against percent atactic polymer. Catalyst systems: (1) δ-TiCl₃AA–AlEt₂Cl; (2) δ-TiCl₃SOL–AlEt₂Cl; (3) δ-TiCl₃HA–AlEt₂Cl; (4) β-TiCl₃–AlEt₂Cl; (5) VCl₃–AlEt₂Cl; (6) CrCl₃–AlEt₂Cl; (7) δ-TiCl₃AA–AlEt₃; (8) δ-TiCl₃AA–AlEt₂Br; (9) δ-TiCl₃AA–AlEt₂I; (10) δ-TiCl₃SOL–AlEt₃; (11) δ-TiCl₃SOL–AlEt₂I; (12) β-TiCl₃–AlEt₂Cl; (13) δ-TiCl₃AA–AlEt₂Cl; (14) δ-TiCl₃AA–AlEt₂Cl; (15) MgCl₂-supported Ti–AlEt₃; (16) MgCl₂-supported Ti–AlEt₃–methyl p-toluate.

correlated with the concentration of the atactic active center. In order to understand this correlation, we have investigated a detailed microtacticity distribution. The samples listed in Table II were fractionated by a temperature-programmed elution column technique.

Microtacticity Distribution of the Polypropylenes Polymerized with the β- and δ-TiCl₃ Catalysts. As seen from Tables I and II, β-TiCl₃–AlEt₂Cl (samples 4 and 12) shows very low stereospecificity (percent atactic polymer; 63%), while δ-TiCl₃–AlEt₂Cl (samples 1, 2, 3, and 13) shows high stereospecificity (percent atactic polymer; <11%).
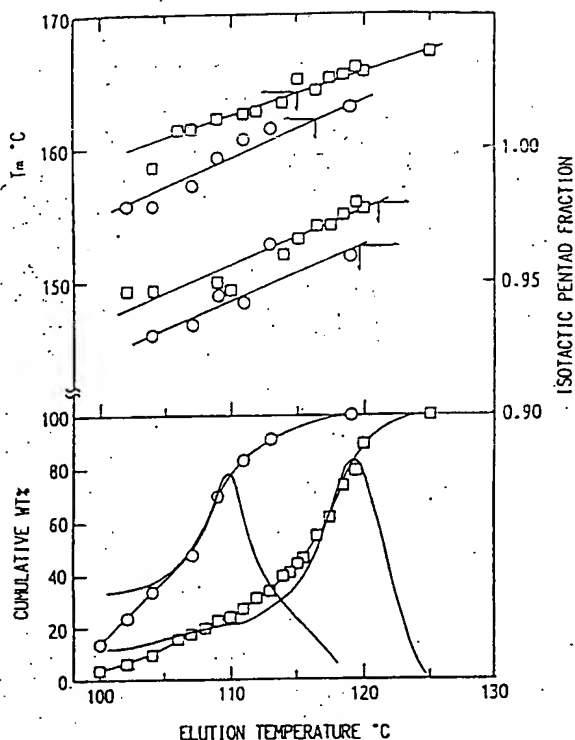
Figure 2. Cumulative and differential fractionation curves and the melting temperatures and the isotactic pentads (*mmmm*) of the fractions. Catalyst systems: (O) β-TiCl$_3$–AlEt$_2$Cl (sample 12); (□) δ-TiCl$_3$AA–AlEt$_2$Cl (sample 13).
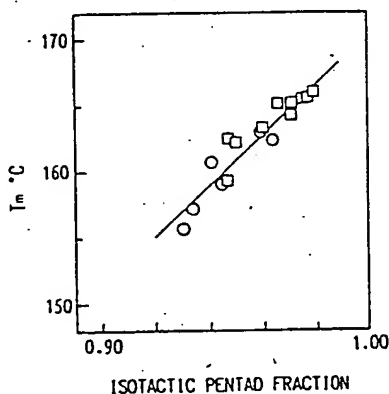

Figure 3. Relationships between the melting temperature (T_m) and the isotactic pentad fraction. Catalyst systems: (O) β-TiCl$_3$–AlEt$_2$Cl (sample 12); (□) δ-TiCl$_3$AA–AlEt$_2$Cl (sample 13).

Furthermore, both catalysts significantly differ from each other in microisospecificity. Thus, the following studies were undertaken to determine the relationship between catalyst structure and the microisotacticity. The cumulative and differential distribution curves in the region of over 100 °C are illustrated in Figure 2, where the melting temperatures and isotactic pentad fractions for the individual fractions are also plotted, both increasing linearly with an increase in elution temperature. These data indicate that the fractionation takes place according to isotacticity as would be expected. The fractionation data clearly show that the polymer (sample 12) prepared with the β-TiCl$_3$ catalyst is a low isotactic polymer compared with that (sample 13) prepared with the δ-TiCl$_3$ catalyst. Next the isotactic pentad fractions of both polymers are plotted against the melting temperatures in Figure 3, where a straight line is given irrespective of a significant difference in molecular weight, 2.5×10^5 for the polymer prepared with the β-TiCl$_3$ catalyst and 3.2×10^5 for that prepared with the δ-TiCl$_3$ catalyst. Accordingly, the iso-
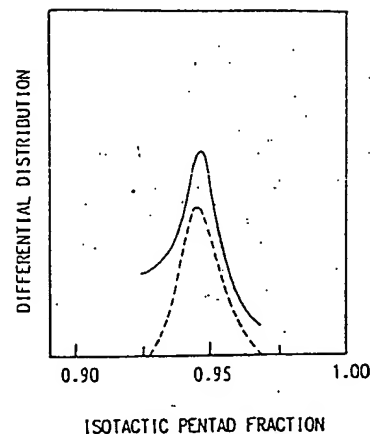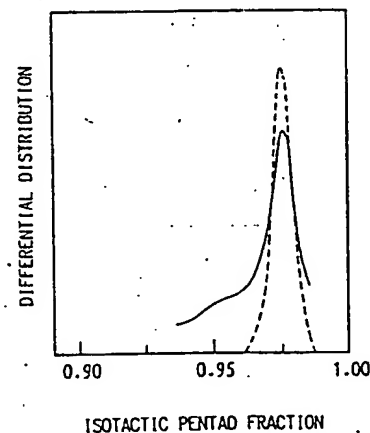

Figure 4. Microtacticity distribution curves. Catalyst system β-TiCl$_3$–AlEt$_2$Cl (sample 12): (—) observed curve; (---) calculated curve ([$mmmm$] = 0.945, M_n = 252 000).

Figure 5. Microtacticity distribution curves. Catalyst system δ-TiCl$_3$AA–AlEt$_2$Cl (sample 13): (—) observed curve; (---) calculated curve ([$mmmm$] = 0.975, M_n = 315 000).

tactic pentad fraction can be determined from the melting temperature. Subsequently the isotactic pentad fraction was determined from the melting temperature by using this relationship.

The stereoregularity of isotactic polypropylene can be expressed by the enantiomorphous model,[1] and therefore, a microtacticity distribution can be calculated on the basis of a binominal distribution. The calculated and observed curves are shown in a differential distribution form in Figures 4 and 5 for the β- and δ-TiCl$_3$ catalysts. Since extremely precise fractionations were achieved, the observed differential curves are believed to be highly reliable. One can see an excellent agreement between the calculated and observed curves in the β-TiCl$_3$ catalyst. This result strongly suggests that the β-TiCl$_3$ catalyst contains only a single isospecific center. On the other hand, two polymers different in microtacticity are observed in the δ-TiCl$_3$ catalyst system: a predominant peak at the isotactic pentad of 0.975 and a discernible shoulder at the region of the isotactic pentad of ca. 0.95. The predominant peak agrees closely with the distribution calculated on the basis of a single active center. However, the shoulder appears to result from another active center. This result suggests that at least two isospecific centers differing in microisospecificity are present in the δ-TiCl$_3$ catalyst.

As shown in Figure 6, the δ-TiCl$_3$ catalyst produces polypropylene with increasingly lower II with the extent of polymerization. At the same time, the microisotacticity also decreases as can be seen from a decrease in the melting temperature. Such change may be explained if the higher isospecific active center decays predominantly. If the
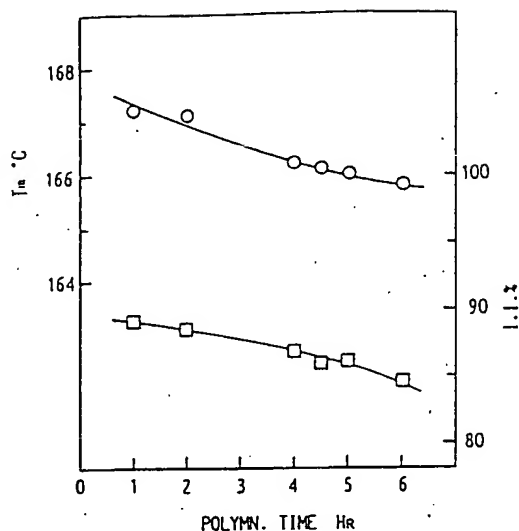
Figure 6. Decrease in the melting temperature (T_m) and the percent II of the polymer with the proceeding of polymerization, catalyst system δ-TiCl$_3$AA–AlEt$_2$Cl. Polymerization conditions: 5-L autoclave; propylene 33 mol; H$_2$ 4 vol %; AlEt$_2$Cl 25 mmol; (O) melting temperature (T_m); (□) percent II.
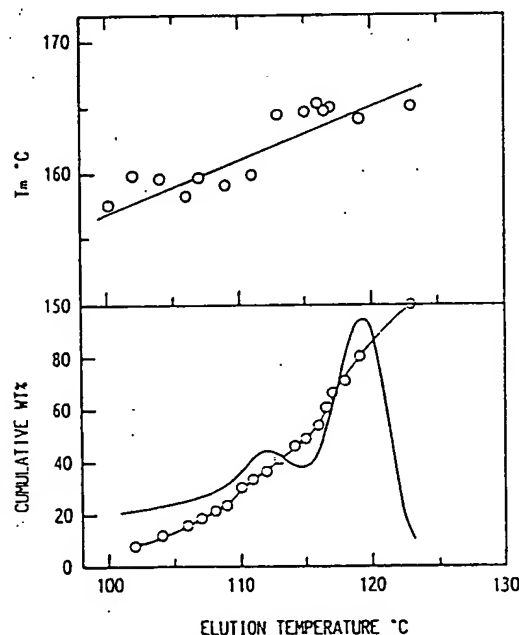

Figure 8. Microtacticity distribution curves. Catalyst system δ-TiCl$_3$AA–AlEt$_2$Cl after aging (sample 14): (—) observed curve; (---) calculated curves ([mmmm] = 0.958, M_n = 84 000 and [mmmm] = 0.975, M_n = 315 000).

Figure 7. Cumulative and differential fractionation curves and melting temperature (T_m) of the fractions; catalyst system δ-TiCl$_3$AA–AlEt$_2$Cl, after aging (sample 14).

Figure 9. Cumulative and differential fractionation curves, and the melting temperature (T_m) of the fractions: (O) MgCl$_2$-supported Ti–AlEt$_3$ (sample 15); (□) MgCl$_2$-supported Ti–AlEt$_3$–methyl p-toluate (sample 16).

assumption is accepted, the low microisotactic polymer should increase in a polymer prepared with an aged catalyst relative to the age of the catalyst. Accordingly, we have examined the polymer (sample 14) polymerized with the δ-TiCl$_3$ catalyst aged for 3.5 h at polymerization temperature (70 °C). As shown in Table II, the aging reduces the polymerization rate. The fractionation results are illustrated in Figure 7, where one can see that the low microisotactic peak is increased relative to the age of the catalyst. This experimental result highly supports the presence of two isospecific active centers. In addition, the decay behavior indicates that they are likely to be chemically different from each other. The microtacticity distribution calculated on the basis of two active centers is shown in Figure 8 together with the observed one. Excellent agreement can be seen between them.

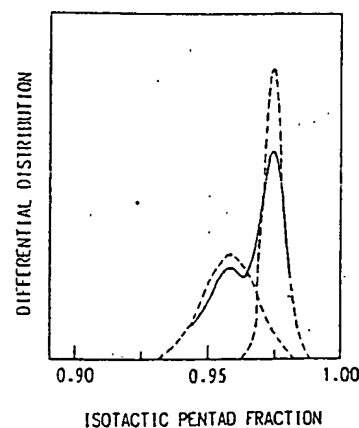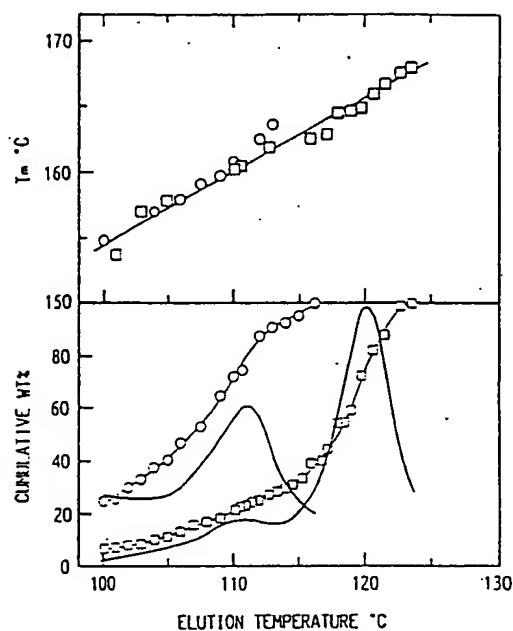**Microtacticity Distribution of the Polypropylenes Polymerized with the MgCl$_2$-Supported Ti Catalyst**

System. The polymers prepared with the MgCl$_2$-supported Ti catalyst systems have been examined in a similar manner. Figure 9 shows the cumulative and differential distribution curves together with the melting temperatures for the polymers polymerized by the MgCl$_2$-supported Ti catalyst with and without methyl p-toluate as an electron donor (samples 15 and 16). In the absence of the electron donor, a single peak is seen at the elution temperature of 111 °C. This elution temperature is close to that of the peak in the β-TiCl$_3$. On the other hand, in the presence of the electron donor, two peaks are seen: a main peak at 121 °C and a small peak at 111 °C. The latter peak is located very close to the peak observed when the electron donor was not added. Figure 10 shows comparisons between the observed and calculated distribution curves for polymers both with and without methyl p-toluate. In each case excellent agreement is found between the observed and the calculated curves.

The conclusion to be drawn from these experimental results is as follows. Only a low isospecific center resides in the low stereospecific catalysts such as the β-TiCl$_3$ catalyst and the MgCl$_2$-supported Ti catalyst without
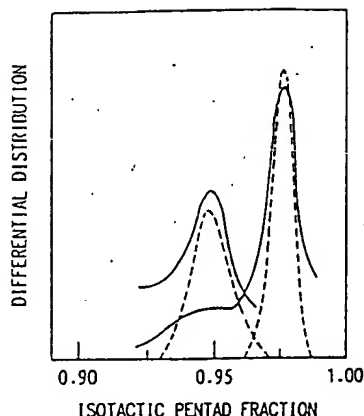
Figure 10. Microtacticity distribution curves. Catalyst system MgCl$_2$-supported Ti: (—) observed curves; (---) calculated curves ([*mmmm*] = 0.949, M_n = 200 000 and [*mmmm*] = 0.976, M_n = 386 000).
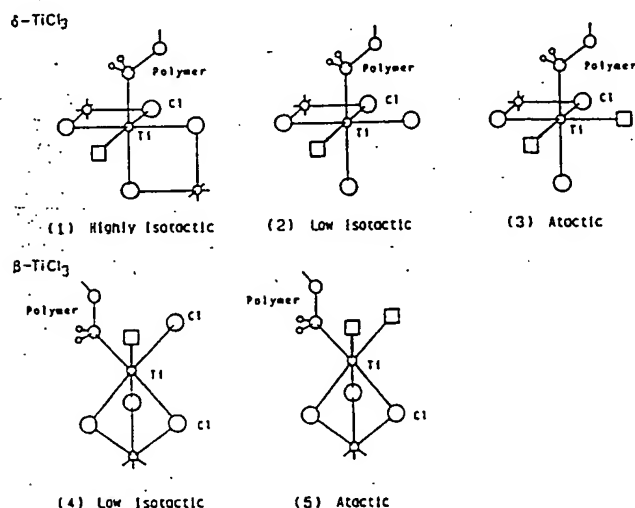

Figure 11. Models for the active centers on β- and δ-TiCl$_3$; (□) Cl vacancy.

electron donor. On the other hand, highly stereospecific catalysts such as the δ-TiCl$_3$ catalyst and the MgCl$_2$-supported Ti catalyst containing the electron donor bear predominantly the highly isospecific center and a small portion of the low isospecific center. The relationship shown in Figure 1 could be accounted for in terms of variation of the proportion of these centers.

Discussion

As described above, β-TiCl$_3$ and δ-TiCl$_3$ significantly differ from each other in both isospecificity and microisospecificity. Such a large difference is presumed primarily to result from a difference in crystal structure. Fortunately, their crystalline structure is well characterized. β-TiCl$_3$ has a linear (chain like) structure, while δ-TiCl$_3$ has a layered structure.[9] According to Arlman and Cossee,[11,12] the isospecific active center in the δ-TiCl$_3$ consists of four firmly bound Cl ions, an alkyl group, and a Cl vacancy (model 1) as shown in Figure 11. On the other hand, β-TiCl$_3$ consists of the chainlike unit. The isospecific center in the β-TiCl$_3$, therefore, may consist of three firmly bound Cl ions, a loosely bound Cl ion, a Cl vacancy, and an alkyl group bound to the Ti atom of the chain end (model 4). From a comparison between two models, the former active center appears to be structurally more rigid than the latter active center because the Cl ions are all bound to Ti atoms. The former active center may therefore possess stronger microisospecificity. The lower iso-
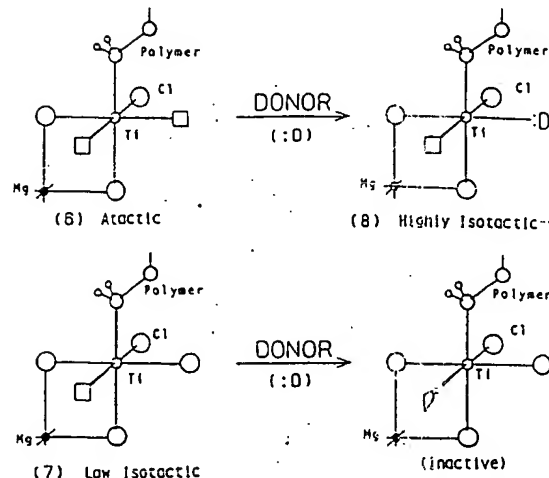

Figure 12. Models for the active centers on supported Ti catalyst and the effect of an electron donor; (□) Cl vacancy.

specific center (isotactic pentad; 0.96) seen in the δ-TiCl$_3$ is close to the isospecific center (isotactic pentad; 0.95) in β-TiCl$_3$ with respect to microisospecificity. The active center, containing a loosely bound Cl ion (model 2) may be attributed to the low isospecific center by analogy with model 4 for β-TiCl$_3$. The active centers having two vacancies (models 3 and 5) probably become nonstereospecific centers.

Judging from the preparation method, the MgCl$_2$-supported Ti catalysts are considered to possess two types of active centers as follows.
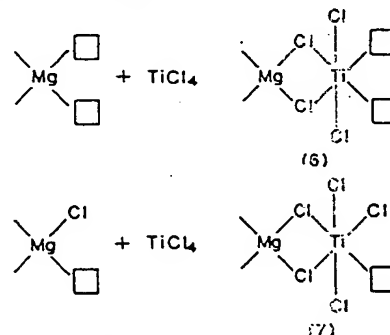
By analogy with β-TiCl$_3$ it seems reasonable that the active center containing two Cl vacancies (model 6) is nonstereospecific and that containing loosely bounded Cl's and a Cl vacancy (model 7) is low isospecific. As shown in Figure 12, the addition of the electron donor may convert the nonstereospecific center to the high isospecific one (model 8), and the low isospecific center to an inactive one.

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Polymerization of Diene-Containing Lipids as Liposomes by Radical Initiators. 4.[1] Effect of Lipid Packing on the Polymerization Profile

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ABSTRACT: 1,2-Di(2,4-octadecadienoyl)-*sn*-glycero-3-phosphorylcholine (DODPC) was polymerized as liposomes with a water-soluble radical initiator, azobis(2-amidinopropane) dihydrochloride (AAPD). DODPC liposomes were prepared with a tip-type sonicator and incubated at 4, 8, or 20 °C. When DODPC liposomes were incubated at lower temperatures than the gel-to-liquid crystalline phase transition temperature (16 °C for DODPC liposomes), these liposomes fused with each other to produce large unilamellar liposomes. An average radius was calculated from the ^{1}H NMR signal intensity ratio for the choline methyl protons split by Eu^{3+}. Generally AAPD initiated radical polymerization of diene groups on the 2-acyl chains of DODPC because of nonequivalent acyl chain packing in bilayer membranes. The polymerization conversion for larger DODPC liposomes reached about 50% by AAPD-initiated polymerization. An excess polymerization was initiated by AAPD when liposomes were not incubated unless the average radius was smaller than 30 nm. This is explained by the disordered lipid packing for small liposomes. This disordered lipid packing permits invasion of water molecules deeper into the hydrophobic region of the outer half of the bilayer membrane of the liposomes, attributed to a larger curvature. For small DODPC liposomes the AAPD radicals could therefore reach diene groups in even 1-acyl chains which were essentially not attacked by AAPD radicals from an aqueous phase as long as lipids were well oriented. The increase of polymerization conversion may be due to an entropically semistable lipid packing inevitable for smaller liposomes. It is concluded that the well-defined selective polymerization of diene groups in 2-acyl chains of DODPC lipids requires liposomes larger in size than with a 30-nm radius.

Introduction

Phospholipid bilayer liposomes are widely applied as microcapsules for drugs or functional molecules as well as models for biomembranes. These liposomes, however, are generally not stable and undergo aggregation and fusion. To stabilize these assembled structures, polymerizable amphiphiles have been incorporated as a major component to construct stable membrane structures by polymerization. In our previous papers, unilamellar liposomes composed of 1,2-di(2,4-octadecadienoyl)-*sn*-glycero-3-phosphorylcholine (DODPC), which contained diene groups in both acyl chains were polymerized by radical initiators.[2,3] Either water-insoluble azobis(isobutyronitrile) (AIBN) or water-soluble azobis(2-amidinopropane) dihydrochloride (AAPD) provided polymerization conversion of around 50% for this lipid. A simultaneous polymerization by these radical initiators resulted in complete polymerization, and the resulting polymerized DODPC liposomes showed excellent stability against physical or chemical stimuli such as sonication or detergent attack.[3] However, this monomeric lipid had polymerizable diene groups in the same position (2,4-diene) in two acyl chains, and it appeared very likely that these acyl chains showed nonequivalent reactivities against water-soluble or -insoluble radical initiators.[3] Polymerization of diene groups bound to the 1-acyl chains was initiated by the addition of AIBN. On the other hand, the diene groups on the 2-acyl chains were believed to face an aqueous phase and were polymerized by the addition of water-soluble radical initiators. This was confirmed by the same polymerization experiments with a monodiene-type polymerizable lipid, 1-palmitoyl-2-(2,4-octadecadienoyl)-*sn*-glycero-3-

phosphorylcholine which possessed one diene group only in the 2-acyl chain. It was clearly demonstrated that the polymerization of diene groups in the 2-acyl chains was initiated only by water-soluble radical initiators.[4] All of the results strongly support the possibility of a selective polymerization of polymerizable amphiphiles in an assembled structure. This selective polymerization, however, was not so clear for very small DODPC liposomes. This suggested that the radical polymerization of these systems should be affected by the lipid packing in the liposomes. This study was therefore intended to elucidate the effect of lipid packing in liposomes on their polymerization profiles.

Experimental Section

Materials. 1,2-Di(2,4-octadecadienoyl)-*sn*-glycero-3-phosphorylcholine (DODPC) was purchased form Nippon Oil & Fats Co., Ltd. This was characterized by thin-layer chromatography (Merck, silica gel plates) with chloroform/methanol/water (65/35/5, by vol) as eluant before use.[3] A polymerizable lipid which showed a single spot on the TLC plate was used without purification. Azobis(2-amidinopropane) dihydrochloride (AAPD) was purchased from Tokyo Kasei Co. Ltd. and was purified by recrystallization twice from water.

Methods. A total of 0.200 g of lipids was dissolved in dry chloroform and was slowly evaporated in a rotating sample tube to prepare a thin lipid film on the inner surface of the tube. Twenty milliliters of degassed distilled water was then added to the tube. The liposome suspension (1.0 wt %) was prepared with a tip-type sonicator (Tomy Seiko UR-200P) at 60 W for 10 min under a nitrogen atmosphere. Freshly prepared liposome suspensions were sealed and incubated at 4, 8, or 20 °C to induce liposomal fusion and to analyze the effect of molecular packing in liposomes upon polymerization. AAPD (3.5 mg; 5 mol % to

Summary: The article discusses two subjects: (a) temperature effects on the molecular weight, molecular weight distribution and stereoregularity of crystalline fractions of propylene polymers prepared with a supported TiCl$_4$/dibutyl phthalate/MgCl$_2$ – Al(i-Bu)$_3$ catalyst system, and (b) effects of different modifiers (components of cocatalyst mixtures that either greatly increase or decrease the content of the crystalline material) on the structures of the crystalline and the amorphous fraction. The principal approach of the research is the combination of GPC data for a series of polypropylene samples prepared under different conditions, the data on the distributional stereoregularity of the polymers (from analytical temperature rising elution fractionation (Tref) and DSC) and the ^{13}C NMR analysis in order to produce a coherent picture of functioning of active centers. The combination of the experimental results shows that the crystalline fractions of polypropylene are produced by several families of active centers. The centers significantly differ in the average molecular weights of the polymer components they produce and in stereospecificity. The steric control exerted by the active centers of the highest isospecificity slightly decreases with temperature. In contrast, average isotacticity parameters of the crystalline fractions (estimated by NMR) increase with temperature. The latter effect is mainly the outcome of the variation in the relative contents of

polymer components of low isotacticity in the crystalline fractions prepared at different temperatures. When a silane is used as a part of a cocatalyst, it not only poisons aspecific centers but poisons the centers of reduced isospecificity as well. This effect results in the increase of the average molecular weight of the crystalline fraction, narrowing of its molecular weight distribution and the increase of its average isotacticity.
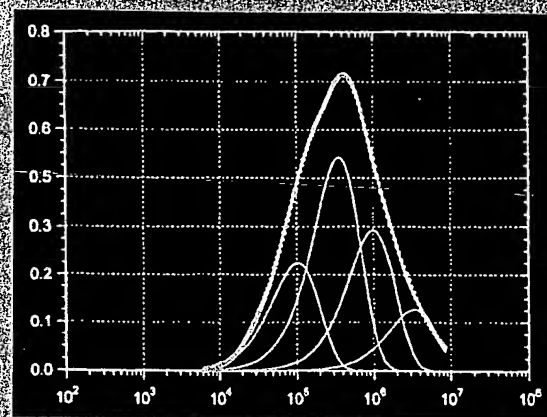
Resolution of GPC curves of crystalline fractions into Flory components at 50 °C.

Propylene Polymerization with Titanium-Based Ziegler-Natta Catalysts: Effects of Temperature and Modifiers on Molecular Weight, Molecular Weight Distribution and Stereospecificity[a]

Dedicated to Professor *Adolfo Zambelli* on the occasion of his 70th birthday

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Introduction

All solid Ziegler-Natta catalyst systems, both the early catalysts utilizing TiCl$_3$ and the modern Ti-based supported

catalysts, contain different families of active centers. Several manifestations of the multi-center nature of the catalysts are observable:

1. All polymers and copolymers produced with these catalysts have broad molecular weight distributions,[1,2]

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[a] 🖳 Supporting information for this article is available on the journal's homepage at http://www.mcp-journal.de or from the author.

in contrast to the polymers prepared with single-center metallocene catalysts that have narrow molecular weight distributions.[1c,2] The molecular weight distributions of the latter polymers is described by a single Flory exponential function.[3] This distribution has a characteristic narrow asymmetric profile in gel permeation chromatograms (GPC),[1a,1b,2,4] and its $\bar{M}_w/\bar{M}_n$ ratio is equal to 2.0.[2,3] Polymer components produced by a single type of active center in multi-center catalysts are commonly called the Flory components. Polymers produced with any heterogeneous Ti-based catalyst consist of at least four or five Flory components.

2. When α-olefins are homopolymerized with these catalysts, different families of active centers produce macromolecules with a different degree of isotacticity.[4,5] Some of the centers are highly isospecific whereas other centers produce fractions of low isotacticity or sterically irregular polymers.

3. When two different α-olefins are copolymerized with these catalysts, different active centers produce copolymer molecules of different compositions.[5j,6]

4. In the course of polymerization reactions, active centers of different types are formed and decay at different rates. As a result, polymer properties, such as molecular weight, molecular weight distribution, stereo-composition, copolymer composition, etc., often vary with reaction time.[5i,6]

5. Active centers of different families can be poisoned or modified with different chemical compounds. This difference in reactivity is widely used for the synthesis of poly(α-olefins) with an improved degree of isotacticity, for the synthesis of predominantly atactic, amorphous poly(α-olefins), as well as for the synthesis of olefin copolymers with a desired degree of compositional uniformity.[2,5d–5f,6,7]

This article discusses two subjects:

1. Temperature effects on the molecular weight, molecular weight distribution and stereoregularity of propylene polymers prepared with a supported TiCl$_4$/dibutyl phthalate (DBP)/MgCl$_2$ catalyst activated with Al(i-Bu)$_3$. In general terms, it is well known that reaction temperature strongly affects the average molecular weight and stereoregularity of polypropylene produced with Ti-based catalysts. Some of these effects were noticed soon after the discovery of the catalysts and, over time, a number experimental results was produced[8–10] and several explanations was proposed to describe the effects.[5a–5c,11] Most of the explanations were related to the nature of chain termination reactions in Ziegler-Natta catalysis and the nature of stereo-errors in predominantly isotactic polypropylene chains.[11b,12] The purpose of the present research is to combine the

analysis of GPC data for polypropylene samples prepared at different temperatures, the data on distributional stereoregularity of the polymers (from analytical temperature-rising elution fractionation (Tref) and DSC), and their ^{13}C NMR analysis in order to produce a coherent picture of functioning of isospecific centers at different temperatures.

2. The second subject of the paper is the examination of the effects of modifiers (components of cocatalyst mixtures) on the molecular weight distribution and the stereospecifity distribution of active centers in the supported Ti-based catalyst.

Historically, two measures have been intermittingly used to describe catalyst stereospecificity. The first one is the fractional stereoregularity of polypropylene, the fraction of polypropylene insoluble either in boiling n-heptane[5a] or in an aromatic solvent (toluene or xylene) at an elevated temperature. This fractionation procedure cleanly separates any crude polypropylene material into a highly crystalline fraction of the predominantly isotactic polymer and an essentially amorphous fraction which was routinely called the atactic material, although its microstructure is quite complex.[11a,13m] The fraction of the insoluble material is usually called "the isotacticity index", but, for the purpose of the following discussion, it is reasonable to define it as fractional isotacticity and to call the respective fractions, however conditionally, as the crystalline and the amorphous fraction (keeping in mind that the crystallinity of the "crystalline" fraction varies depending on reaction conditions and that some components of the "amorphous" fractions can have low crystallinity). The second measure of catalyst stereospecificity is based on spectroscopic analyses, either NMR or IR.[4,8,14] The ^{13}C NMR method has emerged as the method of preference. Over time, its sensitivity has increased and, at the present stage, it routinely affords the measurement of steric heptads and nonads.[12c,13] When these spectroscopic measurements are applied to nonfractionated polymers, the results, for example, the content of mmmm pentads (from NMR) or different IR spectroscopic parameters, usually correlate well with fractional isotacticity and do not provide any principally new information. However, when the ^{13}C NMR measurements are used for characterization of the crystalline fractions, they acquire a new significance: they describe the "quality" of the fractions, the average degree of their deviation from perfect isotacticity,[4,8,11b,14a] as well as the nature of occasional steric defects in isotactic chains.[4,12c,13,15] The main conclusion from the research presented below is that neither of these two measures of isotacticity, the fractional isotacticity or the average isotacticity of crystalline fractions, is sufficient for the mechanistic understanding of propylene polymerization reactions.

Experimental Part

Catalyst and Polymerization Reactions

The supported catalyst[7] was prepared by co-grinding $MgCl_2$ and dibutyl phthalate in a ball mill (25:1 molar ratio) at 20 °C for 60 h followed by a reaction with neat $TiCl_4$ ($[Ti]:[Mg]_{molar} = 7.4$) at 120 °C for 2 h. The solid was filtrated and washed with a large excess of n-heptane; its Ti content was 0.22 $mmol \cdot g^{-1}$. Propylene polymerization experiments were carried out in stainless-steel autoclaves equipped with magnet-driven propeller stirrers, manometers, heating jackets and several ports for introduction of solvents, catalyst components and the monomer. A 1-liter autoclave was used to study the temperature effects. A clean reactor was dried in a nitrogen flow; 380 ml of a reaction medium, n-heptane, was added to it followed by 4 mmol of the cocatalyst, $Al(i\text{-}Bu)_3$. Then the reactor was heated to a desired temperature, the nitrogen atmosphere was replaced with propylene to a total pressure of 8 atm, and then 20 ml of catalyst slurry in heptane containing 44 mg of the solid catalyst was introduced. Polymerization reactions continued for 15 min and were terminated by addition of 30 ml of methanol. Polymer slurries were washed with methanol, filtered and dried under vacuum at 80 °C for 4 h.

To investigate poisoning effects of various modifiers on active centers, the following cocatalyst mixtures were used to control fractional isotacticity of polypropylene:

1. A mixture of $AlEt_3$ (1.0 mmol) and (cyclopentyl)$_2$-$Si(OMe)_2$ at $[Al]:[Si]_{molar} = 8.0$. The polymerization reactions were carried out in the 1-liter autoclave at 80 °C for 1 h in the absence of hydrogen at a total reaction pressure of 8 atm. Productivity of the catalyst system was 295 kg/g Ti × h and the yield of the crystalline fraction was 99.1%.

2. A mixture of $AlEt_3$ (1.5 mmol) and $PhSi(OEt)_3$ at $[Al]:[Si]_{molar}$ of 20. These polymerization reactions were carried out in a 0.5-liter stainless-steel autoclave at 70 °C at different hydrogen partial pressures using a similar catalyst containing 0.5 mmol Ti/g catalyst. Addition of this silane increases the content of the crystalline fraction to ≈96%.

3. A mixture of $AlEt_3$ (4.0 mmol) and 1-allyl-3,4-dimethoxy-benzene (ADMB) at an $[Al]:[modifier]$ molar ratio of 40 and 80. Addition of ADMB greatly reduces the fraction of the crystalline material.[7]

Polymer Characterization

All polymers were separated into crystalline and amorphous fractions by Soxhlet extraction with boiling n-heptane for 16 h. Both fractions were dried under vacuum at 80 °C for 4 h. GPC analysis of polymers was performed at 145 °C with a Waters Model 150C Liquid Chromatograph (five PS columns) using 1,2,4-trichlorobenzene as a solvent. Resolution of GPC curves into Flory components was carried out using the Scientist program (MicroMath Scientific Software), as described elsewhere.[2]

^{13}C NMR spectra of polymers ($0.15 \ g \cdot ml^{-1}$ concentration in a 9:1 1,2,4-trichlorobenzene/$[D_6]$benzene mixture) were recorded with a JEOL JNM-LA-500 NMR spectrometer at 125.6 MHz under proton decoupling. The instrument conditions were: the probe temperature 130 °C, $\pi/4$ pulse at 9 μs, 4.0 s repetition rate, 25 000 Hz sweep width. Deconvolution of overlapping NMR signals of heptads and nonads was carried out with the Scientist program assuming the Lorentzian shape of individual signals.

Analytical Tref measurements were carried out with an Idemitsu-built Tref apparatus equipped with an infrared detector. Polymer samples were loaded from ≈0.5 wt.-% solutions in o-dichlorobenzene on a column with inert packing (Chromosorb P) by cooling the solutions from 135 to 0 °C at a rate of $5 °C \cdot h^{-1}$. The crystallized polymers were held at 0 °C for 30 min and then eluted with o-dichlorobenzene (2 ml $\cdot min^{-1}$) to the IR detector while heating the column from 0 to 135 °C at a rate of 40 °C $\cdot$ h. Deconvolution of overlapping Tref peaks was carried out with the Scientist program assuming that individual Tref peaks have the Lorentzian shape and that the peak width linearly increases with a decrease of the elution temperature.

DSC measurements were carried out with the Perkin Elmer series 7 TA System. The samples were pre-crystallized by melting them at 220 °C followed by cooling at a rate of 20 °C $\cdot min^{-1}$ to 25 °C. The measurements were carried out in the 30–180 °C range at a rate of 5 °C $\cdot min^{-1}$. Polymer crystallinity was calculated assuming $\Delta H_{PP} = 209 \ J \cdot g^{-1}$.[16]

Results

Part A: Temperature Effects

Table 1 contains the principal results of the polymerization reactions: catalyst productivities, the average molecular weights and the molecular weight distributions of the polymers, the contents of crystalline fractions. Similarly to other Ti-based polymerization catalysts,[4,5b,5c] the productivity of the catalyst increases with temperature except for the highest examined temperature when the catalyst decay rate significantly increases. As expected, the average molecular weight of the polymer decreases with temperature. The molecular weight distribution is nearly constant in the 40–70 °C range but decreases at higher temperatures. When the $TiCl_4$/DBP/$MgCl_2$ catalyst is activated with $Al(i\text{-}Bu)_3$ in the absence of a silane modifier, the catalyst system produces polymers with poor fractional isotacticity: the content of the crystalline fraction is 77% at 40 °C and it decreases to 22% at 90 °C. As was mentioned earlier, NMR measurements of unfractionated polymers do not provide additional meaningful information about the stereo-control mechanism. Both the content of the $mmmm$ pentads in the unfractionated polymers and the contents of two major steric defects, $mmrr$ and $mrrm$ steric pentads, change in parallel with the fractional isotacticity. Figure 1 shows examples of these correlations for two cases, the unmodified catalyst and the catalyst modified with AMDB. These changes merely

Table 1. Propylene polymerization reactions with $TiCl_4/DBP/MgCl_2$ catalyst[a] activated with $Al(i\text{-}Bu)_3$[b].

Temperature	Productivity	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Crystalline fraction	$[mmmm]_{av}$
°C	g/g Ti × 15 min			%	%
40	2.2×10^4	8.92×10^5	9.1	77	69.8[c]
50	4.5×10^4	9.05×10^5	10.2	67	70.8[c]
60	3.4×10^4	7.85×10^5	9.2	75	62.1[c]
70	6.6×10^4	6.25×10^5	9.4	57	69.6
80	8.1×10^4	3.28×10^5	6.6	26	56.9
90	7.2×10^4	2.67×10^5	6.4	22	50.2

[a] Heptane slurry containing 44 mg of the catalyst was used in all experiments.
[b] 4 mmol of $Al(i\text{-}Bu)_3$.
[c] Calculated from $[mmmm]$ values of isotactic and atactic fractions.

reflect the fact that the NMR isotacticity parameters of the crystalline and the amorphous fractions are very different: the $[mmmm]$ value is in the 85–95% range for the crystalline fractions and 30–35% for the amorphous fractions. In general terms, all these results are expected for such catalysts; similar trends in catalyst productivity and molecular weight were reported earlier.[10] However, as the data below demonstrate, these general data are totally inadequate for understanding the polymerization catalysis.

Crystalline Fractions: Molecular Weight Distributions

As Table 1 shows, all the polymers are the mixtures of comparable amounts of the crystalline and the amorphous material. The molecular weight distributions of both fractions strongly overlap (see Part D), which precludes any meaningful conclusion about the performance of active centers producing each type of polymer. However, the results for the crystalline fractions are much more informative – see Table 2.
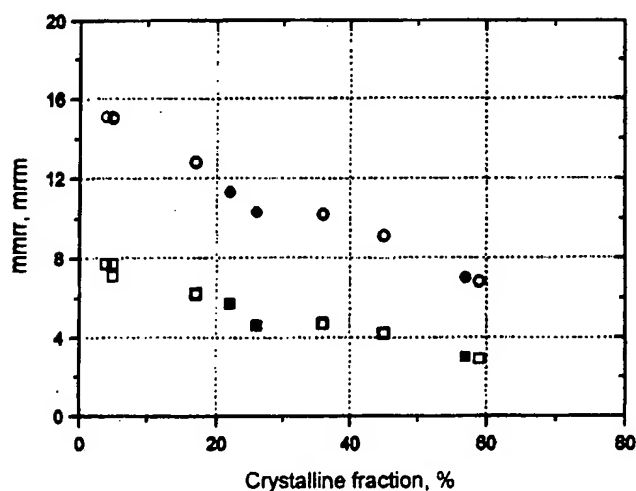

Figure 1. Correlations between contents of two major steric defects in unfractionated polymers and content of crystalline fractions: ● – mmrr, no modifier; ○ – mmrr, ADMB; ■ – mrrm, no modifier; □ – mrrm, ADMB.

Earlier, we have shown that resolution of GPC curves of polyolefins into individual Flory components provides an important insight into the nature of the polymers, both in ethylene[1a,1c,2,6c–6e] and in propylene[2,17] polymerization reactions. Briefly, the goal of the GPC resolution procedure is to determine a minimum number of Flory components (polymer fractions produced by a single family of active centers) which adequately describes a particular GPC curve. Flory curves in the GPC coordinates have a fixed width which is determined by the equation for the Flory

Table 2. Average molecular weights, $\bar{M}_w/\bar{M}_n$ values, and results of GPC resolution for crystalline fractions of polymers prepared with $TiCl_4/DBP/MgCl_2$ – $Al(i\text{-}Bu)_3$ catalyst system at different temperatures.

| Temp.	$\bar{M}_w$ (aver.)	$\bar{M}_w/\bar{M}_n$	Flory component	$\bar{M}_w$(Flory)	Fraction
°C					%
40	901 300	5.60	A	110 400	19.1
			B	389 400	43.1
			C	1 098 200	26.5
			D	3 713 500	11.4
50	831 100	5.69	A	104 300	20.7
			B	358 300	40.7
			C	1 001 600	26.9
			D	3 373 500	11.7
60	767 980	5.52	A	112 600	23.5
			B	363 000	40.2
			C	979 400	24.8
			D	3 369 400	10.5
70	711 300	5.70	A	102 400	25.4
			B	324 260	39.6
			C	921 500	25.4
			D	3 353 300	9.6
80	568 960	5.87	A	104 700	39.8
			B	323 900	38.0
			C	971 400	15.7
			D	3 929 500	6.4
90	564 020	5.86	A	106 300	44.2
			B	410 200	36.3
			C	988 100	14.0
			D	4 102 600	5.6
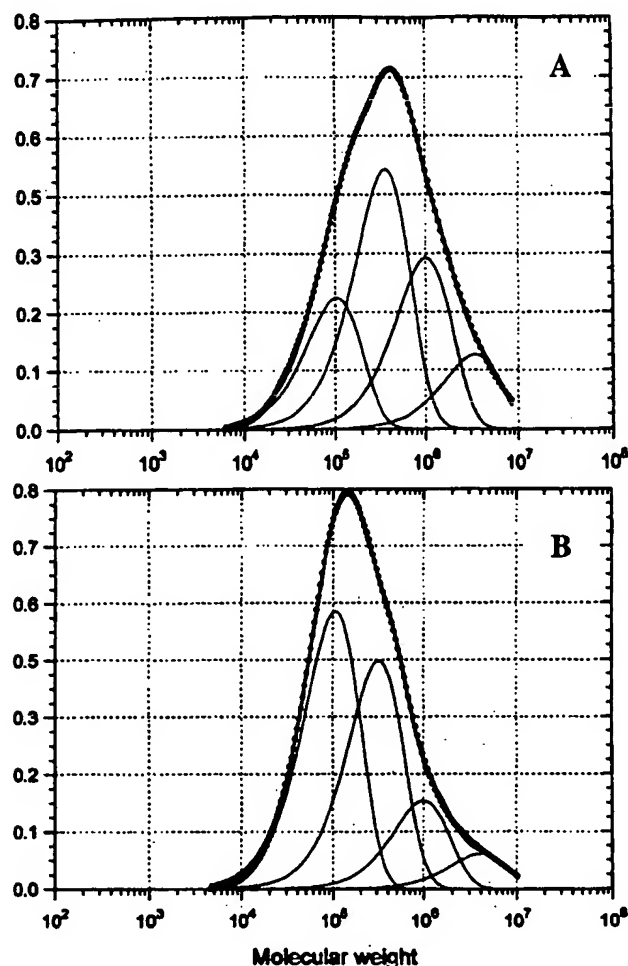
Figure 2.   Resolution of GPC curves of crystalline fractions into Flory components: B – 50 °C, B – 90 °C.

distribution function in the GPC coordinates.[2] Therefore, the curve fitting involves only two parameters, the weight-average molecular weight of each Flory component, $\bar{M}_w$(Flory), and its fraction. Figure 2 shows two examples of the application of this procedure to GPC curves of the crystalline fractions of the polymers prepared at 50 and 90 °C. For brevity, the expression "the family of active centers producing a given Flory component" is replaced below with the expression "a given type of active center".

Generally, the outcome of such GPC resolution procedures can be regarded as the next step in deciphering complexity of multi-center polymerization catalysis. The technique has several limitations:

1. The analysis is based strictly on differences between molecular weights of Flory components. Although some active centers may differ in stereospecificity, they will be inevitably combined in a single group of active centers if the $\bar{M}_w$(Flory) values of the polymers they produce are close.

2. The technique only determines major Flory components. Smaller Flory components, in the 1–3% range, cannot be identified due an unavoidable compromise on the precision of the curve-fitting procedure.

3. Derivation of the equation for the GPC shape of a single Flory component (see examples in Figure 2) depends on linearity of a GPC calibration curve in the "retention time versus log(MW)" coordinates for monodisperse polymers.[2] Deviations from this dependence are sometimes observed in the high-MW range; they affect the quality of fitting as well as $\bar{M}_w$ estimations of Flory components with the highest molecular weights.

Figure 2 shows that each GPC curve consists of four major Flory components. They are marked, in the order of an increasing molecular weight, A through D. Table 2 lists $\bar{M}_w$(Flory) values and contents of the components, as well as the $\bar{M}_w$(average) values of the combined crystalline fractions which were calculated by summation of $\bar{M}_w$(Flory) values of the components. As the polymerization temperature increases, the $\bar{M}_w$(average) value of the crystalline fraction progressively decreases, the same effect as for the unfractionated polymers (Table 1). The width of the molecular weight distribution of the crystalline fraction, the $\bar{M}_w/\bar{M}_n$ value, is virtually independent of temperature.

The data for individual Flory components in Table 2 provide a plausible explanation for the observed $\bar{M}_w$(aver-average) changes. Molecular weights of the Flory components are very different, e.g., the $\bar{M}_w$(Flory) values for components D and A differ by a factor of 35–40. The molecular weight of each Flory component remains approximately the same at different temperatures. What changes with temperature is the contribution of each Flory component to the make-up of a crystalline fraction. As the temperature increases, the fractions of the two components with high $\bar{M}_w$(Flory) values, components C and D, gradually decrease and the fractions of the two components with low $\bar{M}_w$(Flory) values, A and B, increase. This change is the primary reason for the decrease of the average molecular weight of the crystalline fraction with temperature.

The average polymerization degree v_{av}^H of a polymer produced by a single type of active center under usually employed reaction conditions in the presence of a small amount of hydrogen can be sufficiently accurately described by the following equation:[5a–5c,11a]

$$v_{av}^H = k_p \cdot C_{Pr}/(k_{tr}^M \cdot C_{Pr} + k_{tr}^H \cdot C_H) \tag{1}$$

where C_{Pr} and C_H are the concentrations of propylene and hydrogen, respectively, k_p is the chain propagation rate constant, and k_{tr}^M and k_{tr}^H are the rate constants of chain transfer to the monomer (propylene) and to hydrogen. If a polymerization reaction is carried out in the absence of hydrogen, Equation (1) is reduced to:

$$v_{av} = k_p/k_{tr}^M \tag{2}$$

The observation (Table 2) that molecular weights of major Flory components in the absence of hydrogen change little with temperature indicates that the activation energies for the rate constants of the two reactions which determine the $\bar{M}_w$(Flory) values, k_p and k_{tr}^M in Equation (2), are similar.

In general, resolution of GPC curves into Flory components affords identification of two different effects that can account for a gradual change in the average molecular weights of multi-Flory polymer mixtures under varying conditions. These two effects are compared in Figure 3. Figure 3A shows GPC curves of two polypropylene samples prepared at 70 °C in the presence and the absence of hydrogen. These polymers were produced with a TiCl$_4$/DBP/MgCl$_2$ catalyst activated with a mixture of AlEt$_3$ and PhSi(OEt)$_3$. This cocatalyst system affords synthesis of polypropylene containing $\approx 96\%$ of the crystalline fraction. In the presence of hydrogen, the dominant chain transfer reaction is the chain transfer with hydrogen: $k_{tr}^M \cdot C_{Pr} \ll k_{tr}^H \cdot$

C_H in Equation (1). All types of active centers respond to hydrogen approximately to the same degree. As a result, the position of each Flory component shifts, nearly in parallel, toward low molecular weights. This change accounts for the shift of the overall GPC curve in Figure 3A.[17] The width of the molecular weight distribution for the two polymers in Figure 3A changes only slightly: the $\bar{M}_w/\bar{M}_n$ value decreases from 6.5 for the polymer produced in the absence of hydrogen to 5.3 for the polymer produced at a high hydrogen concentration.

In Figure 3B, GPC curves of the two crystalline fractions from Table 2 are compared, one from the polymer produced at 90 °C (its resolution into Flory components is shown in Figure 2) and another at 40 °C. In this case, the reason for the change of the average molecular weight is different. The temperature affects relative contributions of various Flory components (see Table 2); it produces a pronounced change in the curve shape whereas the end-points of the GPC curves remain at approximately the same molecular weights. The two different GPC effects were also noticed in the study of ethylene polymerization reactions with supported catalysts:[6e] $\bar{M}_w$ values of all Flory components in the presence of hydrogen decrease in parallel (as in Figure 3A) whereas the temperature change results in redistribution of fractions of Flory components (as in Figure 3B) while the molecular weights of individual Flory components remain approximately the same.[18]

Crystalline Fractions: Distribution on Stereoregularity

A priori, there is no reason to expect that different Flory components, the materials produced by different families of active centers, have the same stereoregularity. A detailed investigation of this subject can be best achieved with two techniques, analytical Tref (temperature-rising elution fractionation)[5g,5h,19] or crystallization fractionation (Crystaf).[20] Additionally, analyzing DSC data for pre-crystallized polymers provide semi-quantitative information on the stereoregularity distribution.[5g,5i,5k] Various Tref methods were successfully used for detailed characterization of the isotacticity distribution in polypropylene samples prepared with different Ti-based catalysts.[5g–5e,21] The results of the Tref analysis are mainly dependent on stereoregularity and almost independent of molecular weight.[5e,5h,21] This technique reveals even minor differences in stereoregularities of polymers prepared with similar catalysts.[21]

Figure 4A compares analytical Tref curves of the crystalline fractions produced at 40 and 90 °C. First of all, the Tref analysis showed that the Soxhlet separation procedure of crystalline and amorphous fractions with boiling n-heptane is very effective: the contents of the non-crystallizable material (soluble in o-dichlorobenzene at 0 °C) are very small, 1.1% at 40 °C and $\approx 0.1\%$ at 90 °C. Judging by the positions of peak maximums (corresponding to elution
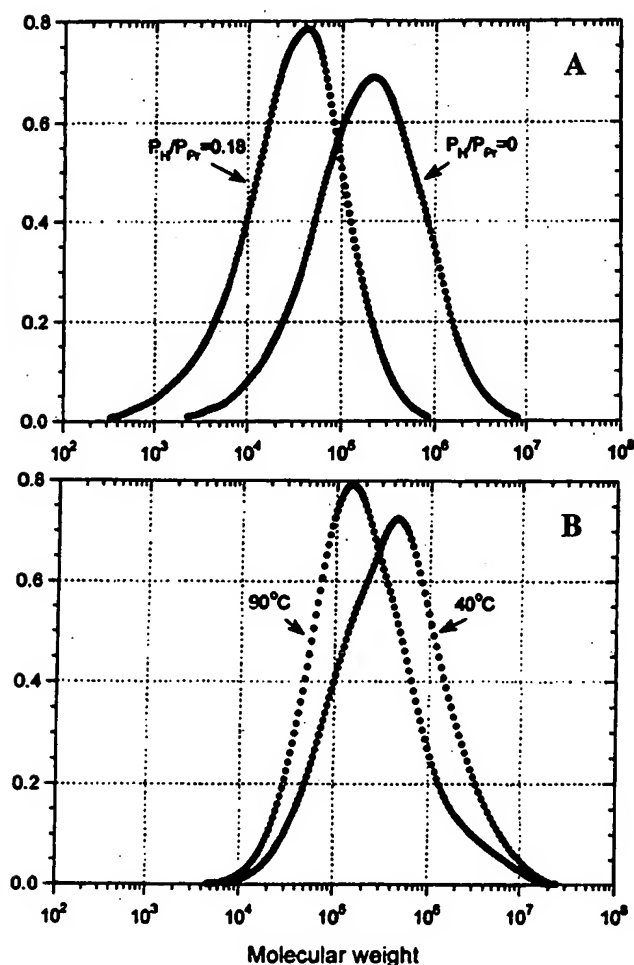

Figure 3. Two manifestations of molecular weight decrease in GPC curves. A: Hydrogen effect, polymers prepared at 70 °C. B: Temperature effect; crystalline fractions prepared at 40 and 90 °C (see Table 1 and 2 for experimental details).
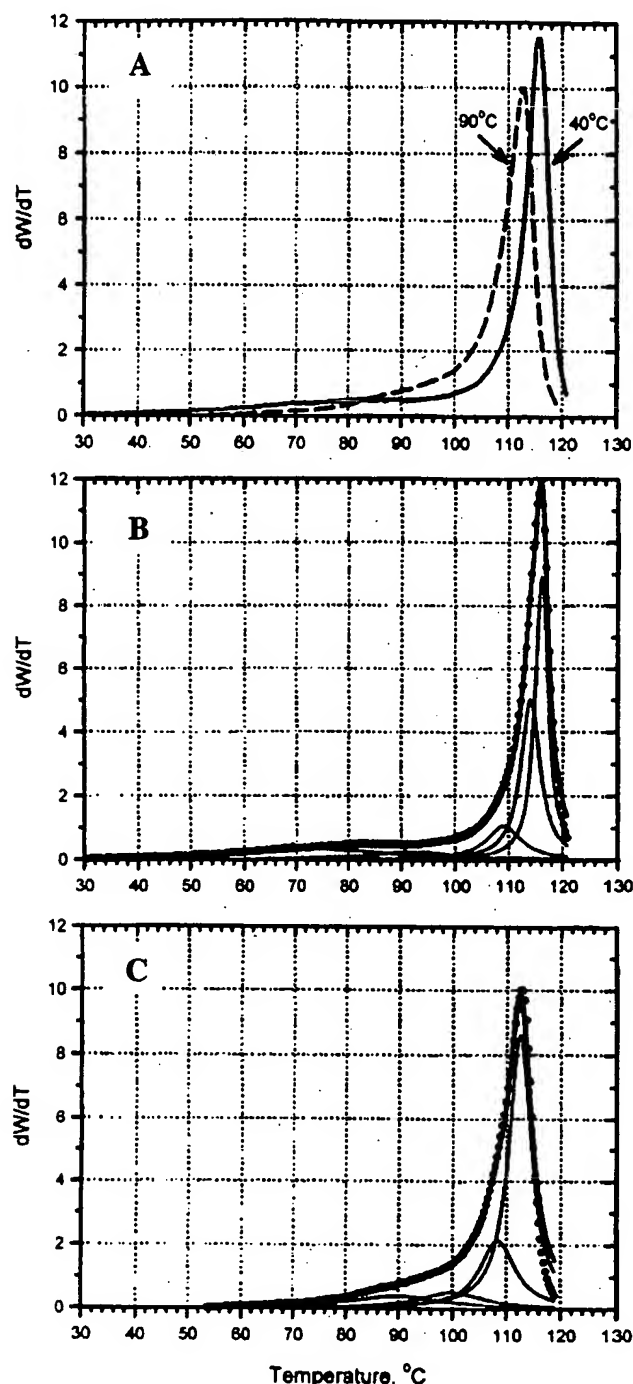
Figure 4. Analytical Tref data for crystalline fractions prepared at 40 and 90 °C (see Table 1 and 2 for experimental details). A: overlap of two Tref curves. Resolution of Tref curves into Lorentzian components: B – 40 °C, C – 90 °C.

temperatures of the bulk of crystalline fractions), the fraction produced at 40 °C contains a more highly isotactic material that elutes at a higher temperature than the material produced at 90 °C: the peaks are at 116 and 113 °C, respectively. However, the crystalline fraction produced at

40 °C also contains a significant amount of a material of low isotacticity eluting in the 90–60 °C range.

Figure 4B and 4C show resolution of both Tref curves into individual components, each described by the Lorentzian shape. This resolution technique is not very precise. Rather, it provides an approximate means of subdividing each crystalline fraction into three components with respect to isotacticity: the highly isotactic fraction (elution peaks in the 110–116 °C range), the fraction of reduced isotacticity (100–110 °C) and the fraction of low isotacticity (75–100 °C). The results are given in Table 3. Tref calibration curves for [mmmm] versus the elution temperature reported in the literature[5i,5j] are nearly linear and afford approximate estimations of [mmmm] values for individual Tref components. They are also given in Table 3. Although these results should be viewed only as semi-quantitative, they show that the crystalline fractions (which are often called "isotactic" fractions) are not uniform and contain polymer components with different levels of stereoregularity, ranging from highly isotactic to materials of quite low isotacticity. The data in Table 3 also reveal complexity of changes in the distribution of active centers with respect to isospecificity as a function of temperature:

1. As the temperature increases, the fraction of the highly isotactic component in the crystalline fraction increases from ≈65 to ≈80%.
2. The temperature change has a relatively small effect on the "quality" of this highly isotactic component; its [mmmm] value slightly decreases at the higher temperature.
3. The component of low isotacticity is present in both crystalline fractions. Its content decreases by half in this temperature range, from ≈20 to ≈10%.

DSC analysis, by its nature, is especially sensitive to the properties of polymer components with the highest crystallinity (and, therefore, the highest isotacticity). The DSC melting curves of the 40 °C and 90 °C crystalline fractions are compared in Figure 5. The position of the curve maximum for the 40 °C fraction is slightly higher (155.8 °C) compared to that of the 90 °C fraction (155.1 °C). This difference suggests a slightly higher isospecificity of the "best" isospecific centers in the catalyst at the lower temperature, the same conclusion as that from the Tref analysis (Table 3). However, the total crystallinity of the 90 °C fraction is slightly higher, 51% versus 48% for the 40 °C fraction. A comparison with the Tref results in Table 3 shows that this difference is due to a higher content of the polymer component of low isotacticity in the crystalline fraction prepared at 40 °C.

Crystalline Fractions: ^{13}C NMR Stereoregularity Data

The data on the isotacticity distribution in the previous section call for a very cautious approach to the NMR

Table 3. Resolution of Tref curves of crystalline fractions prepared with $TiCl_4/DBP/MgCl_2$ – $Al(i\text{-}Bu)_3$ catalyst system at two temperatures.

Temp.	Component	T_{max}	$[mmmm]$[a]	Fraction
°C		°C		%
40	Highly isotactic	116.1, 114.0	≈0.96 (av.)	≈66
	Moderately isotactic	109.0	≈0.94	≈12
	Low isotacticity (1)	≈92	≈0.82	≈7
	Low isotacticity (2)	≈70	≈0.64	≈15
90	Highly isotactic	112.4, 108.4	≈0.95 (av.)	≈80
	Moderately isotactic	99.9	≈0.92	≈9
	Low isotacticity	≈89	≈0.78	≈11

[a] Approximate evaluation based on calibration in ref.[5j]

analysis of crystalline polypropylene fractions. All NMR-based values of stereoregularity, by their nature, give the average rather than the distributive information on the types and the contents of various steric errors in complex polymer mixtures. In a situation when different components of crystalline fractions have different molecular weights (Table 2) and different isotacticities (Figure 4B and 4C, Table 3), it is unwarranted to assume that different types of steric mistakes observed by NMR (although their contents are always low) belong to the same polymer chains.[22]

Positions of ^{13}C NMR signals in various steric sequences in polypropylene are well known from the literature, starting with the pioneering works of A. Zambelli and his coworkers[15] and continuing up to the present time.[12c,13] When ^{13}C NMR spectra are recorded at 125.6 MHz, the measurement of the contents of steric pentads is straightforward. Several spectral areas also afford a reasonably accurate measurement of steric heptads. The mrrm range (19.8–20.1 ppm) and the rrrr range (20.2–20.5 ppm) are specially suitable for the purpose due to comparatively large differences in the chemical shifts between signal

positions of longer steric sequences. Figure 6 gives two examples of signal resolution in these ranges for the polymer produced at 40 °C. Relative positions of the heptad signals produced by the curve-fitting method match well the
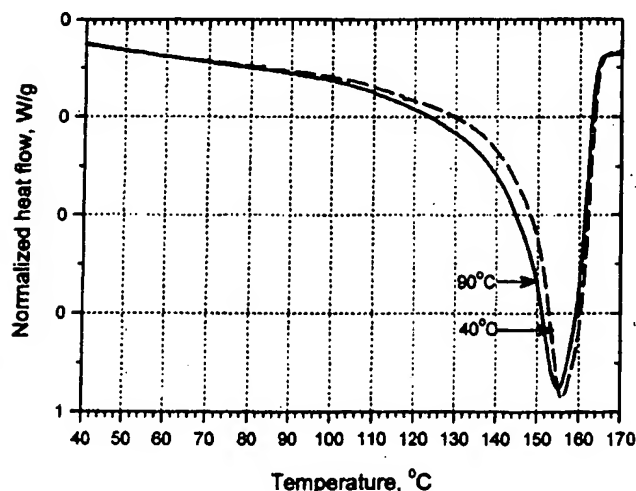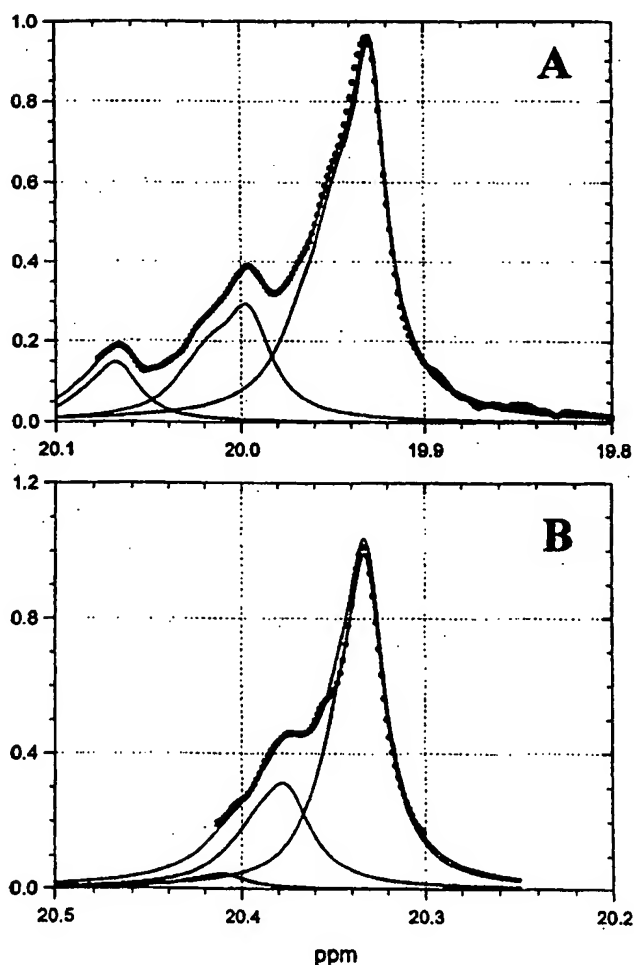

Figure 6. Heptad resolution of two CH_3 signal ranges in the ^{13}C NMR spectrum of the 40 °C crystalline fraction. A: the mrrm range, B: the rrrr range.

Figure 5. DSC melting curves of crystalline fractions prepared at 40 and 90 °C.

published data.[13f,13j,13m] Each heptad signal has a pronounced asymmetry due to small differences in the positions of *mrrm*-centered nonads, *mmmrrmmm* versus *mmmrrmmr* versus *rmmrrmmr*.

Detailed interpretation of the NMR spectra of predominantly isotactic polypropylene is a complicated subject. Strictly empirically, all the CH_3 signals (see Table 1A in Supplementary Information) can be separated into three categories:

1. Signals of imperfect isotactic sequences: the main signal of the *mmmm* pentads and the signals of common steric errors, *mmmr*, *mmrr* am *mrrm* pentads (and respective heptads, as discussed below). These are the dominant sequences in all samples in Table 1.
2. Signals of predominantly syndiotactic steric sequences: *rrrrr*, *rrrrrm*, *mrrrrm*, *rrrrmr* heptads, etc.
3. Signals of various sterically irregular sequences.

There are two alternative approaches to explaining coexistence of these steric sequences in one polypropylene sample. The first approach, pioneered by Randall and Busico,[12e,13e,13h,23] assumes that several changes can occur in the stereo-control mechanism at some active centers during the lifetime of a single macromolecule. Such a hypothetical center produces, in succession, isotactic, syndiotactic and atactic blocks of various lengths connected one to others. The second approach to explaining the structural diversity of stereo-errors in polypropylene chains proposes co-existence of two different types of stereospecific active centers in the catalysts, both producing crystalline materials. Most of the centers are highly isospecific and produce predominantly isotactic polymer molecules with a few steric defects predicted by the enantiomorphic stereo-control model (Scheme 1, Equation (3); see discussion below, Section C). Other centers, a minority, produce

a crystalline, predominantly syndiotactic polymer. In addition, because the separation of the crystalline and the amorphous fractions is not perfect, the crystalline fractions usually contain small admixtures of atactic polymer chains.

The principal subject of this research is stereoregularity of active centers that produce predominantly isotactic polymer chains (or, alternatively, the active centers at the stage when they produce long, predominantly isotactic sequences). Table 4 gives contents of *meso*-pentads [*mmmm*] in the crystalline fractions of the polymers prepared at 40, 70, 80 and 90 °C. The contents of all stereo-sequences in these samples are given in Table 1A in Supplementary Information. From the formal standpoint, the ^{13}C NMR results are clear: as the temperature increases from 40 °C to 90 °C, the average NMR isotacticity of the crystalline fraction increases: the *mmmm* pentad content increases from 83 to 91% and the contents of all major stereo-errors, *mmmr*, *mmrr* and *mrrm*, decrease (Table 1A). This formal evaluation matches well the previously published results in the same temperature range, NMR data by Chadwick et al.[10] and IR data by Rishina et al.[8]

Obviously, a disagreement exists between the Tref data (Table 3) and the DSC data on one hand and the NMR data in Table 4 on the other hand. Both the Tref and the DSC results show that the isotacticity degree of the "best" isotactic material in the crystalline fractions slightly decreases with temperature whereas the average NMR data in Table 4 show the opposite effect. The nature of this disagreement can be clarified if another commonly used method for varying the content of the crystalline fraction, the use of silane modifiers, is examined.

Part B: Effects of Silane Modifiers on the Structure of Crystalline Fractions

Addition of alkyl- or arylalkoxysilanes to organo-aluminium cocatalysts is the universally practiced technique for the increase of the fraction of crystalline polypropylene produced with supported $TiCl_4$/dialkyl phthalate/$MgCl_2$ catalysts. The primary effect of the silane is a sharp decrease in the content of the amorphous fraction, from 30–50% to

A single steric error in an isotactic chain (enantiomorphic model):

$$m\ m\ m\ m\ m\ m\ r\ r\ m\ m\ m\ m \qquad (3)$$

Two possible types of steric errors in syndiotactic chains:

$$r\ r\ r\ r\ r\ r\ m\ r\ r\ r\ r \qquad (4)$$

$$r\ r\ r\ r\ r\ r\ m\ m\ r\ r\ r\ r \qquad (5)$$
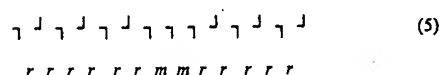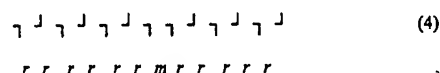
Scheme 1.

Table 4. Contents of *meso*-pentads in crystalline fractions of polymers prepared with $TiCl_4$/DBP/$MgCl_2$ – Al(*i*-Bu)$_3$ catalyst at different temperatures[a].

Temperature	[*mmmm*]
°C	%
40	83.4
70	88.1
80	89.2
90	91.2

[a] Experimental conditions for polymer synthesis are in Table 1.

less than 2–4%.[24] This effect is most probably achieved by selective poisoning of aspecific active centers. In addition, the silanes affect both the molecular weight distribution and the stereo-distribution of the crystalline fractions.

Effects of Silanes on Molecular Weight Distribution

Figure 7A shows GPC curves of two crystalline fractions prepared with the same supported catalyst at 80 °C. One of the polymers was produced with Al(i-Bu)$_3$ (see Table 1) and the second one with AlEt$_3$-(cyclo-C$_5$H$_{11}$)$_2$Si(OMe)$_2$ mixture at [Al]:[Si]$_{molar}$ = 8. The GPC curves are very different indicating a strong modifying effect of the silane on isospecific centers. The weight-average molecular weight of the polymer nearly doubles as a result of the silane addition. Figure 7B and 7C show resolution of both GPC curves into Flory components and Table 5 gives parameters of the components. A comparison of Figure 7B and 7C and analysis of the data in Table 5 affords a relatively straightforward explanation of the silane effect. The silane significantly reduces the relative activity of center A, and, to a smaller degree, center B. On the other hand, the silane does not affect the molecular weight of any Flory component (the precision of the $\bar{M}_w$ estimation of the Flory components in the curve-fitting calculations is not very high, ±10–15%) and it does not affect the ratio between the contents of components C and D. Earlier, one of us reported the same silane effect in propylene polymerization with the TiCl$_4$/DIBP/MgCl$_2$ catalyst activated with a AlEt$_3$ – Ph$_2$Si(OMe)$_2$ mixture.[2] This silane effect is also similar to its effect in ethylene/α-olefin copolymerization reactions.[2,6b]

Effect of Silane on ^{13}C NMR Stereoregularity of the Crystalline Fraction

Table 6 compares ^{13}C NMR isotacticity parameters of the crystalline fractions of the two polymers, one cocatalyzed with Al(i-Bu)$_3$ and another with the AlEt$_3$- (cyclo-C$_5$H$_{11}$)$_2$Si(OMe)$_2$ mixture. Only the most significant steric errors are listed, all other steric errors are present in too low amounts to be dependably measured. The overall silane effect is obvious: the modification not only increases the content of the crystalline fraction from 26 to 99% but it also noticeably improves the average NMR isotacticity of the fraction. (The presence of the silane does not affect much the content of the syndiotactic sequences, see below.) A comparison of the GPC data in Table 5 and the NMR data in Table 6 strongly suggests that Flory components A and B have a lower stereoregularity than components C and D.

Part C. The Simplest Statistical Model for Individual Flory Components in Crystalline Fractions

One of the principal goals of the present research is analysis of the temperature effect and the effect of silane modifiers
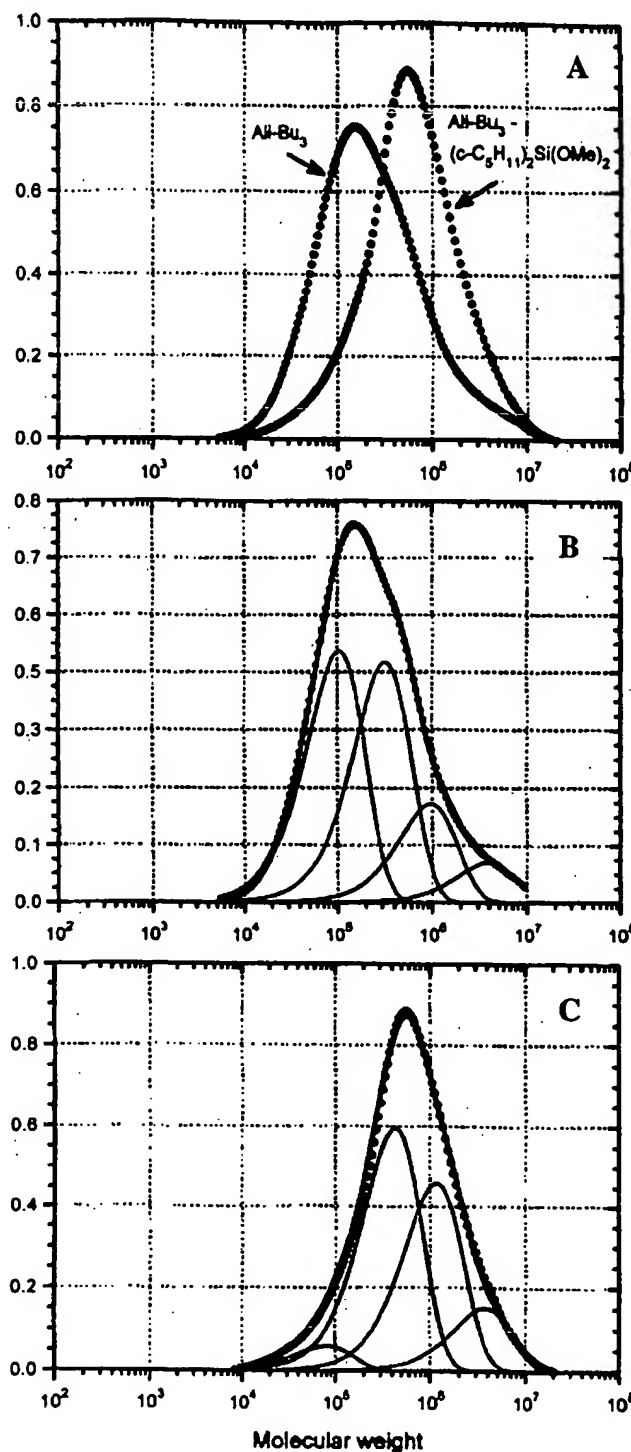

Figure 7. GPC curves of crystalline fractions of polypropylene prepared at 80 °C without and with silane modifier. A: Overlap of the GPC curves. Resolution of GPC curves into Flory components: B – no silane, C – (C$_5$H$_{11}$)$_2$Si(OMe)$_2$ at [AlEt$_3$]:[Si]$_{molar}$ = 8.0.

on the isospecific active centers. The combination of the results in previous sections is the basis of the following model: (a) the crystalline fractions are produced by several types of active centers, and (b) all the centers are isospecific

Table 5. Average molecular weights, $\bar{M}_w/\bar{M}_n$ values and results of GPC resolution for crystalline fractions of polymers prepared at 80 °C with TiCl$_4$/DBP/MgCl$_2$ catalyst activated with different cocatalysts.

Cocatalyst	$\bar{M}_w$ (aver.)	$\bar{M}_w/\bar{M}_n$	Flory component	$\bar{M}_w$(Flory)	Fraction %
Al(*i*-Bu)$_3$	568 960	5.87	A	104 670	39.8
			B	323 890	38.0
			C	971 380	15.7
			D	3 929 550	6.4
AlEt$_3$-(*cyclo*-C$_5$H$_{11}$)$_2$Si(OMe)$_2$	1 074 200	4.34	A	≈90 000	4.7
			B	430 750	47.0
			C	1 166 650	36.3
			D	3 708 600	12.0

Table 6. Silane effect on average stereoregularity and some chain defects in crystalline fractions of polymers prepared at 80 °C with TiCl$_4$/DBP/MgCl$_2$ catalyst.

Cocatalyst	[*mmmm*]	[*mmmr*]	[*mmrr*]	[*mmrm + rrmr*]	[*rrrr*]	[*mrrm*]
Al(*i*-Bu)$_3$	89.2	3.55	3.78	0.63	0.37	1.63
AlEt$_3$-(*cyclo*-C$_5$H$_{11}$)$_2$Si(OMe)$_2$	97.8	1.25	0.93	0.15	0.30	0.32

but they differ in the degree of isotacticity of polymer molecules they generate (as well as their average molecular weight). Two subjects present the most interest:

1. Developing a simple kinetic measure of stereo-control for a single type of an isospecific active center.
2. Explanation of the contradiction between two measures of stereoregularity of crystalline fractions produced at different temperatures, one derived from Tref and DSC results (Table 3, stereoregularity of macromolecules produced by the "best" isospecific centers is nearly constant in the 40–90 °C range) and from the NMR data (Table 4, stereoregularity increases with temperature).

Fortunately, the content of syndiotactic sequences in the crystalline fractions of our polymers is relatively small, from 0.5 to 1.5% (see Table 1A in Supplementary Information) and their presence does not interfere with the first task of statistical analysis, finding a kinetic measure of stereo-control and its estimation from the contents of *mmmm* pentads and major steric errors in isotactic chains.

Simple Enantiomorphic Model

In a situation when different types of isospecific active centers produce Flory components with different amounts of stereo-defects (as the data in Section A show) it appears prudent to limit statistical analysis for a single type of active center to the simplest stereo-kinetic model of the isotactic chain growth, the enantiomorphic model.[14,25] The standard example of an isolated steric error in the isotactic chain is shown in Scheme 1, Equation (3), together with its description in terms of steric links between neighboring

monomer units according to the Bovey classification.[26] In terms of steric pentads, the sequence in Equation (1) contains only three types of steric errors, *mmmr*, *mmrr* and *mrrm*, in the 2:2:1 ratio. A few minor steric errors can also develop when such isolated steric errors are, by chance, situated relatively close one to another. Recently, a more complex stereo-control mechanism was proposed for propylene polymerization with C$_1$-symmetric *ansa*-metallocene complexes, which also leads to predominantly isotactic polymers.[27] Both mechanisms are experimentally indistinguishable in the case of highly isospecific centers.[12b]

In the simplest case,[4,5c,14a] both the probability of the steric error (formation of the first *r* link in Equation (3)) and the probability of recovery after the error (formation of the second *r* link) do not depend on the configuration of the preceding monomer unit in the chain. A single parameter is used for calculating frequencies of various steric errors in imperfectly isotactic chains, the ratio of two propagation rate constants, $R_{iso} = k_{iso}/k_{syndio}$, one leading to the prevailing monomer placement (k_{iso}) and another to the steric error (k_{syndio}). The necessary equations for this simplest statistical model, correlations between contents of various steric sequences and R_{iso} values, are given in Table 2A in Supplementary Information. When the R_{iso} value is estimated from NMR data (which give average [*mmmm*] values and average contents of steric errors in crystalline fractions) the R_{iso} value is also an average value for families of several centers that differ in the level of stereospecificity.

The total content of major steric errors in polypropylene chains in our samples is small (see Table 4, Table 6 and Table 1A in Supplementary Information) and a single type

Table 7. Estimations of R_{iso} values (the simplest enantiomorphic model) for crystalline fractions of polymers prepared at different temperatures.

Pentad	R_{iso} at			
	40 °C	70 °C	80 °C	90 °C
[mmmm]	27	39	43	54
[mmmr]	35	44	50	55
[mmrr]	36	45	47	59
[mrrm]	40	50	57	62

of steric error shown in Equation (3) should represent it in a satisfactory fashion. Table 7 gives estimations of average R_{iso} values for the crystalline fractions prepared at different temperatures. These estimates were derived both from the [mmmm] values (Table 4) and from the contents of major steric defects (Table 1A in Supplementary Information). Of course, the trend for the average R_{iso} values is the same as for the [mmmm] values in Table 4, but the R_{iso} values change in a relatively small range in this temperature range. In contrast, the change in the average R_{iso} value for the crystalline fractions prepared without and with the silane modifier is very large, from ≈50 to ≈200. This change suggests that the isospecific centers responsible for the formation of Flory components C and D produce nearly perfectly isotactic macromolecules and centers A and B produce material of significantly lower isotacticity.

Possible Explanation for Opposite Temperature Trends in Isotacticity from Tref and NMR

The ambiguousness of the estimations of average R_{iso} values for elucidation of a stereo-control mechanism becomes apparent when the R_{iso} values derived from contents of different steric mistakes measured for the same polypropylene sample are compared. For the crystalline fraction prepared at 90 °C, all R_{iso} estimations are relatively high and the R_{iso} values derived from the contents of mmmr, mmrr and mrrm pentads are all quite close – see Table 7 (the precision of these estimates is no better than ±5%). However, when these R_{iso} values are used to calculate relative ratios of various mrrm-centered heptads expected from the enantiomorphic model (using equations in Table 2A), a lack of inter-correlation between different NMR measures of

stereospecificity becomes obvious. Data in Table 8 show that the experimentally determined fractions of heptads corresponding to two and three closely positioned steric errors, ~mmrrmr~ and ~rmrrmr~, are much higher than those expected from the enantiomorphic statistics. Two alternative explanations can be proposed to account for this discrepancy:

1. The frequency of steric errors is governed by a peculiar chain growth mechanism when the chance of a steric error is greatly, 5–10 times, increases at the third position after the preceding steric error.
2. More reasonably, different mrrm-centered heptads do not belong to the same chain.

Examination of the literature data showed several other examples of such a lack of inter-correlations between high R_{iso} values estimated from the contents of mrrm pentads on one hand and high [mmrrmr]:[mmrrmm] ratios on the other hand. The examples include crystalline fractions of polypropylene prepared with the δ-TiCl$_3$-AlEt$_2$Cl system,[13f] the TiCl$_4$/MgCl$_2$-Al(i-Bu)$_3$ system,[13j] and the TiCl$_4$/MgCl$_2$/2,6-Me$_2$-pyridine-AlEt$_3$ system.[13i] In contrast, highly isotactic polypropylenes produced with isospecific single-center metallocene catalysts have only a narrow signal of the mmrrmm heptads, in accordance with the simple enantiomorphic statistics represented by Equation (3).[28] These observations suggest that, indeed, three different mrrm-centered heptads in crystalline fractions of polypropylene produced with Ti-based catalysts, mmrrmm, mmrrmr and rmrrmr, belong to different polymer chains. The mmrrmm heptad describes the "normal" isolated error in highly isotactic chains (Equation (3) in Scheme 1) whereas mmrrmr and rmrrmr heptads characterize chains of lower isotacticity, which are also present in the crystalline fractions but produced by active centers of reduced isospecificity (see Table 3). Correspondingly, the estimations of R_{iso} values in Table 7 are averages of quite broad distributions of active centers with respect to R_{iso}, as the data in Figure 4 and Table 3 testify.

As was mentioned earlier, the R_{iso} values for the crystalline fraction prepared with the silane-modified cocatalyst calculated from [mmmr], [mmrr] and [mrrm] values are very high, ≈200–210. According to any stereo-control model, polypropylene chains with such a low content of steric errors should have only isolated errors represented by

Table 8. Experimental and calculated ratios between three mrrm-centered heptads. The calculations are based on R_{iso} values estimated from [mrrm].

	[mmrrmm]:[mmrrmr]:[rmrrmr] at			
	40 °C	70 °C	80 °C	90 °C
Calculation	1:0.050:0.00064	1:0.040:0.00041	1:0.035:0.00031	1:0.032:0.00026
Experiment	1:0.34:0.12	1:0.26:0.04	1:0.19:0.05	1:0.17:0.02

Equation (3) and are not expected to have sizable fractions of these errors situated close one to another. For example, the expected [*mmrrmm*]:[*mmrrmr*] ratio for $R_{iso} \approx 200$ is $\approx 100:1$. However, when the ^{13}C NMR spectrum of the crystalline fraction produced with the silane-modified cocatalyst was analyzed, resolution of signals in the *mrrm* range into heptads using the same procedure as shown in Figure 6 (although it is quite imprecise due to the very low overall content of the *mrrm* pentads) gave a much lower [*mmrrmm*]:[*mmrrmr*] ratio, $\approx 4:1$. These results again can be interpreted as the indication that this crystalline fraction contains a small component of polymer chains of relatively low isotacticity, which mostly contribute to the contents of *mmrrmr* and *rmrrmr* heptads. The nature of this component can be deduced from Figure 4 and Table 3. The extraction of the polymer mixture prepared at 40 °C with boiling *n*-heptane leaves in the solid fraction 15% of a material of quite low isotacticity, with [*mmmm*] of ≈ 0.6. The presence of this material results in a significant decrease of the average [*mmmm*] value for crystalline fractions produced at lower temperatures (as estimated by NMR, Table 4) although isospecificity of the "best" isospecific centers is really slightly higher at lower temperatures.

Part D: Amorphous Fractions of Polypropylene

Fractions of polypropylene soluble in boiling *n*-heptane can be called amorphous only conditionally. These fractions are very complex mixtures of macromolecules which differ both in molecular weight and stereoregularity. Figure 8A shows the GPC curve of the unfractionated polymer prepared with the unmodified catalyst at 80 °C (see Table 1) and the GPC curves of its two fractions drawn in scale. The amorphous fraction has a very broad molecular weight distribution and the average molecular weights of both fractions do not differ much one from another. The GPC curve of this amorphous fraction was also separated into Flory components. The results are given in Table 9. As a minimum, five Flory components are required to describe the molecular weight distribution of this fraction in a quantitative manner. It should be kept in mind that in the case of such complex polymer mixtures resolution of GPC curves into Flory components is, to a significant degree, a formal procedure. Some of these "components" are the overlaps of several Flory components with different stereoregularities but which happen to have similar molecular weights.

Amorphous Fractions: Molecular Weight Distributions. Effect of ADMB

1-Allyl-3,4-dimethoxybenzene (ADMB) is an effective modifying agent for Ti-based supported catalysts.[7] It suppresses active centers producing isotactic polypropylene chains: the content of the crystalline fraction at 80–
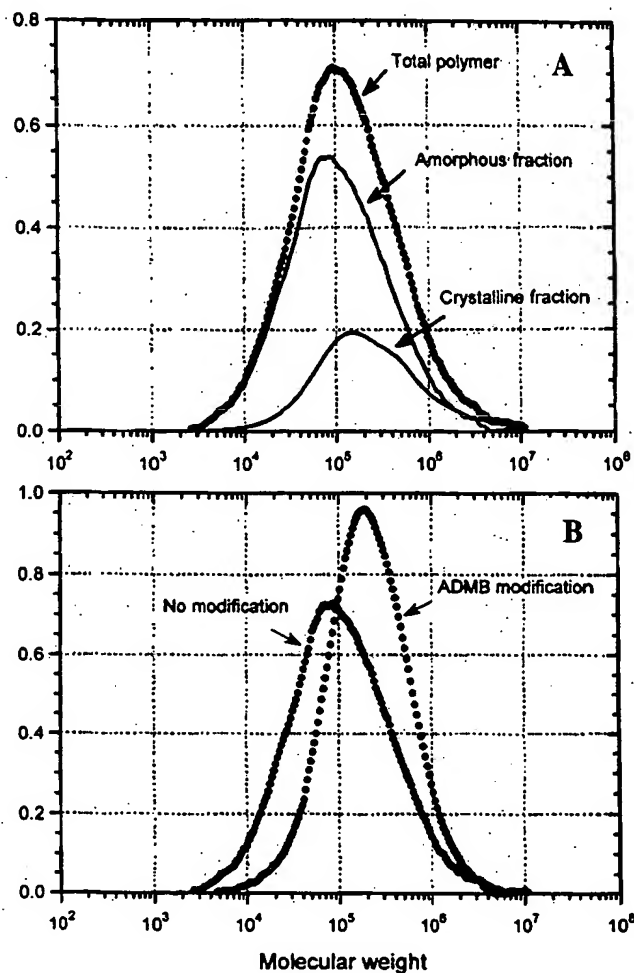

Figure 8. GPC curves of amorphous fractions of polymers produced at 80 °C. A: Polymer prepared with unmodified catalyst and its crystalline and amorphous fractions. B: Amorphous fractions, unmodified catalyst and catalyst modified with ADMB.

90 °C decreases from ≈ 25 to 4–5%. The second effect of ADMB becomes apparent when GPC curves of the amorphous fractions prepared in its presence and absence are compared – see Figure 8B. Addition of ADMB results in significant narrowing of the molecular weight distribution of the amorphous fraction, mostly due to the loss of its low molecular weight components. This effect is quantified in Table 9 for two pairs of polymers produced at 80 and 90 °C. The designation of Flory components in the table as A′, B′, etc., is arbitrary, they are not related to Flory components A, B, etc., in the crystalline fractions. The data show that introduction of ADMB results in complete elimination of components A′ and B′ whereas components C′, D′ and E′ are preserved in approximately the same ratios. As a result, the average molecular weight of the amorphous material produced with ADMB increases and its $\bar{M}_w/\bar{M}_n$ value decreases.

Table 9. Average molecular weights, $\bar{M}_w/\bar{M}_n$ values and results of GPC resolution for amorphous fractions of polymers prepared with TiCl₄/DBP/MgCl₂ catalyst.

Temp.	Cocatalyst	$\bar{M}_w$ (aver.)	$\bar{M}_w/\bar{M}_n$	Flory component	$\bar{M}_w$(Flory)	Fraction
°C						%
80	Al(i-Bu)₃	217 600	5.12	A′	20 100	5.6
				B′	55 300	33.1
				C′	138 900	33.5
				D′	374 200	21.4
				E′	1 108 600	6.4
	Al(i-Bu)₃-ADMB	343 400	3.16	A′, B′		0
				C′	141 100	47.0
				D′	377 600	43.0
				E′	1 238 900	9.2
90	Al(i-Bu)₃	185 200	5.25	A′	17 600	8.4
				B′	61 300	44.0
				C′	155 400	25.7
				D′	321 500	16.5
				E′	1 199 900	5.3
	Al(i-Bu)₃-ADMB	278 500	3.10	A′, B′		0
				C′	125 400	55.2
				D′	344 800	38.3
				E′	1 180 900	6.5

Amorphous Fractions: ^{13}C NMR Stereoregularity

Due to steric heterogeneity of amorphous polypropylene fractions, their ^{13}C NMR spectra are very complex and futility of their structural NMR analysis in terms of a single statistical model has been understood quite early.[13m] Potentially, the amorphous material prepared with ADMB has an advantage in this respect because, at least, it has a much more narrow molecular weight distribution that may translate into a more uniform stereochemical distribution. Figure 9 shows resolution of two ranges in its ^{13}C NMR spectrum, those of *mrrm* and *rrrr* pentads, into their constituent heptads. The *mrrm* data can be compared with the data for other sequences characteristic for polymer chains of low isotacticity and to evaluate, however approximately, the average isospecificity of the respective active centers. The estimations are based on the ratios of relative contents of various sequences expected for predominantly isotactic polymer chains (see Table 2A in Supplementary Information). They are given in Table 10. Although the spread of the R_{iso} values is quite high (which can be expected of such a complex polymer mixture), the main conclusion is that ≈70% of all observed signals in the ^{13}C NMR spectrum of the amorphous fraction can be assigned to poorly isotactic sequences characterized by an average R_{iso} value of 4 (±20%) rather than to purely atactic sequences when, by definition, $R_{iso} = 1$.

Part E: Syndiotactic Components in Crystalline and Amorphous Fractions

Existence of long syndiotactic sequences in polypropylene mixtures prepared with Ti-based Ziegler-Natta catalysts has

been known since 1960;[29] it has been extensively studied by NMR.[12b,13f-i,13m,25c,30] The main manifestation of these sequences is the presence of the signals of *rrrrrr*, *rrrrrm* and *mrrrrm* heptads in the ^{13}C NMR spectra – see Figure 6 and 9. The presence of *rmrrrr* and *rrmrrr* resonances in the ^{13}C NMR spectrum of the amorphous fraction (it corresponds to a single error in a syndiotactic chain (Equation (4) in Scheme 1) and the virtual absence of the *rrmmrr* resonance that corresponds to a different type of steric error (Equation (5)) indicates that the formation of these syndiotactic sequences can be approximately described by the chain-end control mechanism of chain growth.[4,5c] The same stereo-defects are present in the syndio-rich fractions of polypropylene produced with a TiCl₄/MgCl₂ catalyst activated with an AlEt₃ – Ph₂Si(OMe)₂ mixture.[5k] The statistical parameter defining the stereo-regulating power of syndiospecific active centers, $R_{syndio} = k_{syndio}/k_{iso}$, can be estimated[4] from the contents of the two most prominent heptads: $[rrrrrm]:[rrrrrr] = 2R_{syndio}^{-1}$. The results are presented in Table 11.

They show that:

1. The stereo-regulating power of the syndiospecific centers is quite low: the R_{syndio} value is ≈6 at 40 °C and decreases to ≈2.5 at 90 °C.

2. Plotting R_{syndio} data for syndiotactic sequences in the crystalline fractions in the Arrhenius coordinates gives a very approximate estimation of the ΔE_{act} value for the rate constants of syndiotactic versus isotactic monomer addition at these centers, ≈−3.0 kcal · mol⁻¹.

3. R_{syndio} values for syndiotactic sequences in the crystalline and the amorphous fractions prepared at the same

Discussion

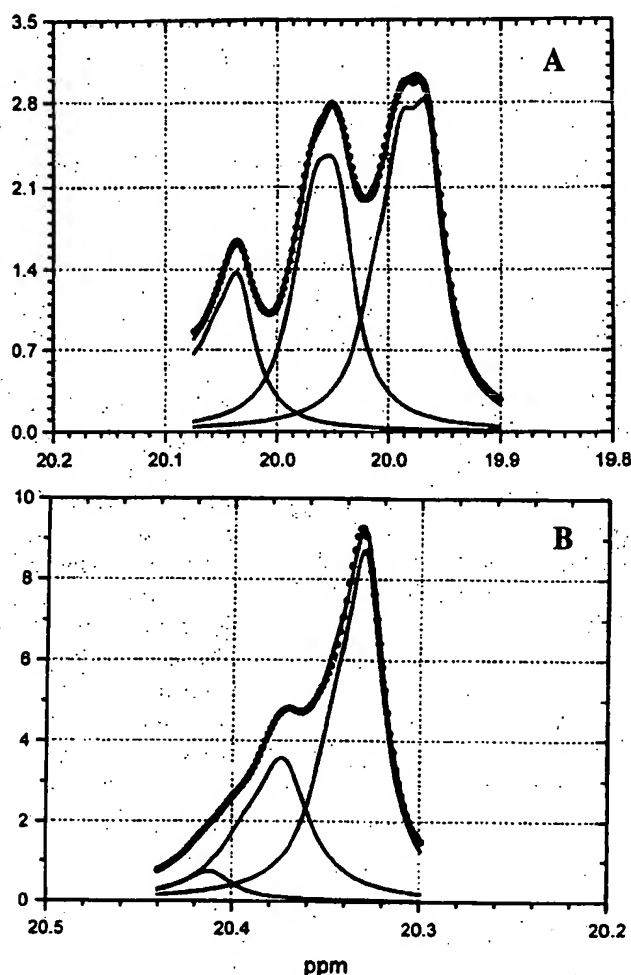The data on the fractional content, the molecular weight distribution, the stereo-composition distribution, and NMR stereoregularity of crystalline and amorphous fractions of polypropylene prepared with $TiCl_4/DBP/MgCl_2$ catalyst activated with pure $Al(i-Bu)_3$ at different temperatures and with $AlEt_3$/modifier cocatalyst mixtures give a relatively coherent picture of the catalyst functioning. It is common to assume that active centers in such catalysts can be broadly divided into two groups, highly isospecific active centers that produce the crystalline fraction and centers of a much lower isospecificity producing mixtures of macromolecules which have a greatly reduced crystallinity or are completely amorphous (see their fractions in Table 1). The combination of the GPC, Tref and NMR data gives a much more nuanced picture. The crystalline polypropylene fractions cannot be viewed as uniform materials. Judging by their molecular weight distributions, they are produced by several families of active centers (centers A-D in Tables 2 and 5). The centers differ in the values of rate constant ratios k_p/k_{tr}^M (see Equation (1) and (2)) giving rise to different molecular weights of respective Flory components. These families of centers significantly differ in isospecificity as well (Table 3, Figure 4 and 5). Although a detailed correspondence between the Tref and the GPC results is still not possible, our data provide semi-quantitative information about the differences in isotacticities of different Flory components. Two effects should be considered:

1. When the polymerization temperature increases, the contents of Flory components A and B in the crystalline fractions increase (Figure 3B, Table 2) and the "steric perfectness" of the material with the highest isotacticity slightly decreases (Figure 4 and 5, Table 3).
2. When a silane is used as a modifier, the fraction of components A and B decreases (Figure 7B, Table 9) and the average NMR-derived isotacticity degree of the crystalline fraction increases (Table 6).

The combination of these data indicates that Flory components A and B have lower stereoregularities compared to components C and D. Only an approximate estimation is possible: at 80 °C, the [mmmm] value for Flory component A is ≈76% whereas it is ≈99.5% for components C and D. This difference translates into a very large difference between the stereo-regulating powers of the respective centers: the R_{iso} ratio is ≈20 for center A and ≈1 000 for center D.

The data in Figure 4 show that a single-solvent Soxhlet extraction technique, although quite adequate for many practical purposes, has a drawback when applied to polymers containing large high molecular weight fractions. The extraction of the polymer prepared at 40 °C failed to remove from the polymer mixture a significant fraction,

Figure 9. Heptad resolution of two CH_3 signal ranges in the ^{13}C NMR spectrum of the amorphous fraction prepared at 80 °C in the presence of ADMB. A: the *mrrm* range, B: the *rrrr* range.

temperature are close. Taking into account the multi-component nature of both the crystalline and the amorphous fraction, one can assume that the mechanism of the preferred syndiotactic chain growth is the same in both cases.

Table 10. Estimations of R_{iso} values (the simplest enantiomorphic model) from ^{13}C NMR data for the amorphous fraction of polymer prepared at 80 °C with $TiCl_4/DBP/MgCl_2$ – $Al(i-Bu)_3$/ADMB catalyst.

Source	Value	R_{iso}
[mmmr]:[mmmm]	0.42	4.8
[mmmr]:[mmmm]	0.58	3.5
[mrrm]:[mmmm]	0.28	3.7
[mmrrmm]:[mmmm]	0.13	5.7
[rrmmrr]:[mmmm]	0.046	3.8
[mmrrmr]:[mmrrmm]	0.75	2.8

Table 11. Estimations of R_{syndio} values for of syndiotactic chain growth from NMR data.

Temperature	Crystalline fractions				Amorph. fraction	
	40 °C	70 °C	80 °C	90 °C	80 °C[a]	80 °C
[rrrrrr]:[rrrrrm]	1:0.32	1:0.45	≈1:0.51	≈1:0.8	1:≈0.4[b]	1:0.54
R_{syndio}	≈6.2	≈4.4	≈3.9	≈2.5	≈5[b]	≈3.7

[a] Data for silane-modified catalyst.
[b] Estimation is quite imprecise due to very low signal areas.

≈15%, of the component of low isotacticity, with [mmmm] of ≈0.6. The presence of such materials results in an artificial decrease of the NMR-derived average [mmmm] values for the crystalline fractions produced at low temperatures (Table 4). This effect may explain the contradiction between two opposite temperature effects on isospecificity of the active centers:

1. The distributive data derived from Tref and DSC indicate that the stereo-regulating control of the centers of the highest isospecificity is either constant of slightly decreases with temperature (Figure 4 and 5, Table 3).
2. The cumulative measurements of isotacticity, both in this research (from NMR data, Table 4) and in the literature (by NMR or IR),[8,10] suggest that the average isotacticity of the crystalline fractions increases with temperature. This change is mostly an outcome of temperature variations in the contents of Flory components produced by the centers of a lower isospecificity and it is not related to the performance of particular active centers.

It is instructive to compare this temperature invariance of the steric control of the "best" isospecific centers in Ti-based catalysts with the temperature effect on another family of isospecific catalysts, bridged metallocene complexes. The first article by Kaminsky et al. on propylene polymerization with the bridged metallocene complex $C_2H_4(Ind)_2ZrCl_2$ showed that as the temperature increases the IR isotacticity of the polymer noticeably decreases.[31] More recently, Rytter et al.[32] studied propylene polymerization with the $Me_2Si(Ind)_2ZrCl_2$ – MAO system at a high [Al]:[Zr] ratio of 5 000, a prerequisite for single-center catalysis.[2] This catalyst produces predominantly isotactic polymers but, as the temperature increases from 40 to 90 °C (the same range as in our experiments), the [mmmm] value progressively decreases from 92 to 49%. This trend is paralleled by a drastic decrease of the melting point of the polymers, from 142.5 to 83.0 °C. Similar temperature effects on NMR isotacticity and melting points were observed in the case of $Me_2Si(2-Me-Ind)_2ZrCl_2$,[32] $C_2H_3Ph(9-Flu)_2ZrCl_2$,[33] $Me_2Si(2-Me-Benz[e]Ind)_2-ZrCl_2$,[34] and other bridged metallocene complexes.[35] The degree of stereo-control in the case of syndiospecific

$Ph_2C(Cp)(9-Flu)ZrCl_2$-based catalysts also noticeably deteriorates with temperature.[36] In contrast, our data (Figure 5) show that the peak melting points of isotactic fractions prepared at 40 and 90 °C differ by less than 1 °C. This comparison shows that isospecific active centers in solid Ti-based catalysts are much more rigid than metallocenium ions (bridge)$(Cp')(Cp'')Zr^+$-R.

The presence of syndiotactic sequences in the predominantly isotactic polymers in the crystalline fractions, as well as in all amorphous fractions, was the subject of many discussions.[12a-c,12e] The amount of the syndiotactic material depends on the nature of the catalyst. It is present in quite high amounts in polypropylene produced with the $TiCl_3$ – $GaEt_3$ system[30d] and in some fractions of polymers produced with a $TiCl_4/MgCl_2$ – $AlEt_3$ catalyst modified with methyl-substituted piperidines[12b,13h,13i,23] whereas it is virtually absent in polymers produced with the α-$TiCl_3$ – $AlEt_3$ system.[30d] Two alternative opinions exist in the literature about the nature of the syndiotactic material:

1. Syndiotactic macromolecules are formed, independently of the isotactic material, on special active centers in Ti-based catalysts. Indeed, the syndiotactic fractions can be relatively cleanly separated from the bulk of the isotactic material, either in multi-stage fractionation procedures[5k,5e,29,30b,37] or chromatographically.[29]
2. Relatively long syndiotactic blocks are present in the same macromolecules as long isotactic blocks due to a change of a stereo-control mechanism at a given active center during the lifetime of a single macromolecule.[12e,13e,13h,23]

The amounts of rrrr sequences in the polymers prepared in the present experiments are too low to discriminate between these two possibilities (Table 4). Our data merely indicate that the syndiospecific stereo-control is quite weak (Table 11), in contrast to the isospecific stereo-control, and that it rapidly deteriorates with temperature.

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Effect of internal donors in propylene polymerization analyzed with the two-site model

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Abstract: The effect of internal donors of Ziegler-Natta catalyst on stereoregularity in propylene polymerization was analyzed with the aid of the two-site model analysis system. The amount of internal donor and that of external donor were varied. The probability in the selection of d (or l) monad in asymmetric site is contributed by both the amount of internal donor and that of external donor. With respect to the fraction of asymmetric site, the two-site model enabled us to conceive that the new kinds of active centres are generated in specific cases where external donor is believed to be replacing weaker internal donor during polymerization. The effect of hydrogen concentration during polymerization is also discussed.
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Keywords: two-site model; Ziegler-Natta catalyst; internal donor; propylene polymerization; stereoregularity

INTRODUCTION

Since the discovery of Ziegler–Natta catalyst, isotactic polypropylene has been widely used as commodity material due to its low cost and excellent physical properties. As the modulus of the resin is closely related to isotacticity, understanding the polymerization mechanism is important in the chemistry of propylene polymerization as well as in industry.

NMR has been one of the most powerful analytical tools for determining the microstructure of polypropylene since 1962.[1] Many attempts have been made to describe statistically the formation of isotactic polymer chains,[2] and the two-site model[3] is widely accepted as 'the best' stochastic model of olefin polymerization. This model has been proven valid not only for polyolefins but also for vinyl-type polymers such as polystyrene. The model is especially useful to describe the polymerization mechanism by using pentad fractions of the ^{13}C NMR spectra of polyolefins. This model is effective in obtaining a better understanding of the nature of the polymerization centres for propylene.

In the area of isotactic polypropylene, there have been several publications[4–6] in which the two-site model stochastic parameters are successfull in explaining the effect of external donors which are used in combination with solid catalyst component. However few studies employing the two-site model have been made on the effect of internal donor in catalyst component.

In this study, the authors focused on the effect of internal donors on stereoregularity of Ziegler–Natta

catalyst systems with the aid of the two-site model analysis system now also available through the internet.[7,8†]

BRIEF REVIEW OF THE TWO-SITE MODEL PARAMETERS

The theory and parameters of the two-site model are presented elsewhere in detail,[3] but the model is briefly reviewed here for convenience. This model is composed of three parameters: these are stochastic parameters describing the role of the first and the second sites, and the fraction of the polymers obtained from the first site. More precisely, the first parameter, α, is the probability of the selection of d (or l) monad in an asymmetric site; the second one, σ, is that of m diad in a symmetric site; and the last one, ω, is the fraction of polymers obtained from an asymmetric site. Therefore, $(1-\omega)$ denotes the fraction of polymers obtained from symmetric site.

The reason why we limited the number of parameters to three is based on the number of experimentally obtained values. ^{13}C NMR spectra of polypropylene with recent catalyst systems give only four pentads that can be observed with sizeable intensities: they are mmmm, mmmr, mmrr and mrrm. Because of normalization conditions, three parameters against four experimental values should become the number of independent variables.

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† The internet site is available for free access and use except for telecommunication fee.

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Table 1. The catalysts and the internal donors

Catalyst identifies	Internal donor[a]	Donor content $(mmol\,g^{-1})$	Ti content $(mmol\,g^{-1})$	iD/Ti (molar ratio)
1a	DEP	0.06	0.25	0.24
1b	DEP	0.22	0.34	0.65
1c	DEP	0.36	0.41	0.88
2a	DBP	0.03	0.31	0.10
2b	DBP	0.10	0.37	0.27
2c	DBP	0.18	0.37	0.49
3a	DOP	0.03	0.39	0.06
3b	DOP	0.09	0.44	0.21
4a	EB	0.06	0.29	0.19
4b	EB	0.27	0.40	0.69
4c	EB	0.29	0.44	0.67
5a	DE	0.02	0.36	0.06
5b	DE	0.19	0.48	0.39
5c	DE	0.26	0.56	0.47

[a] DEP, diethyl phthalate; DBP, di-*n*-butyl phthalate; DOP, di-*n*-octyl phthalate; EB, ethyl benzoate; DE, 9,9-bis(methoxymethyl)fluorene.

EXPERIMENTAL
Catalyst preparation
Magnesium chloride (30 g, SA 11 m² g⁻¹) and internal donor were placed in a 1-l stainless steel vibration mill pot with 50 balls (25 mm diameter) under nitrogen and vibrated at room temperature for 30 h. The ground product (10 g as $MgCl_2$) was reacted with $TiCl_4$ (200 ml) in a 500-ml flask twice for 2 h each time at 110 °C, followed by washing with *n*-heptane. The types of internal donor as well as the amount were varied to obtain a series of solid catalyst components. The Ti content was determined by titration with iron (III) sulfate after reduction with aluminium. The donor content was determined by GC using a toluene

extract of catalyst. The Ti and donor content analyses are summarized in Table 1.

Propylene polymerization
The propylene polymerization was carried out in a 2.0-l stainless steel autoclave. In the presence of small amount of *n*-heptane, $Al(C_2H_5)_3$ (1.32 mmol) and an external donor, cyclohexylmethyldimethoxysilane (Si) were placed in the autoclave, and then catalyst (2.6 μmol Ti) was introduced at room temperature. After hydrogen (2.0 or 6.0 l) had been charged, liquid propylene (740 g) was introduced and prepolymerization was conducted at 20 °C for 5 min. The temperature was then raised to 70 °C, and polymerization was conducted at 70 °C for 60 min. Typically, about 300 g of polypropylene powder was obtained. The results were summarized in Table 2.

¹³C NMR measurement
¹³C NMR measurements were made only for the *p*-xylene insoluble fraction, since the physical properties of PP are mainly determined by isotactity of the insoluble fraction. ¹³C NMR spectra of the polymers were obtained on a JEOL GSX-270 spectrometer using 10 mm OD tubes. Sample concentration was about 5 wt% in 1,2,4-trichlorobenzene/C_6D_6. The chemical shifts were referenced to TMS.

The results were analyzed using the internet system for two-site model analysis.

RESULTS AND DISCUSSION
The effects of the internal donor and external donor on α
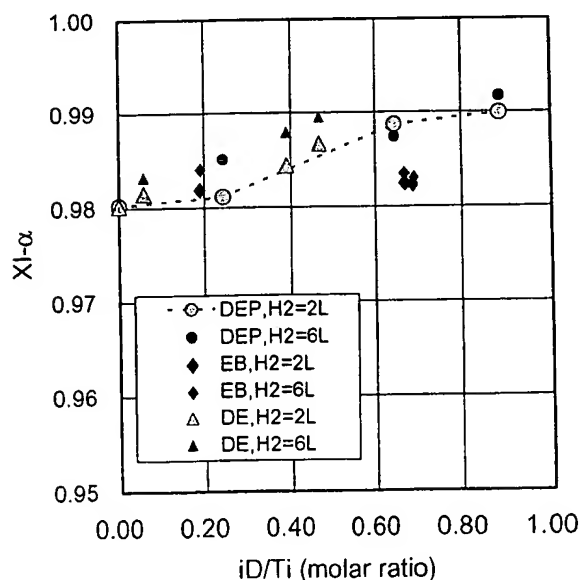Figure 1 shows the relationship between mmmm and

Catalyst identifies	Si/Ti (mol/mol)	Activity (g PP/g catalyst)	p-XI[a] (wt%)	XI fraction		
				mmmm (mol%)	α	ω
1a	0	14 100	43.0	81.8	0.968	0.965
	10	14 500	76.9	89.3	0.981	0.983
	50	12 700	87.3	92.8	0.987	0.989
1b	0	18 800	61.8			
	10	23 600	92.1	92.9	0.989	0.983
	50	21 600	94.7	93.7	0.989	0.989
1c	0	30 500	61.0	85.6	0.976	0.966
	10	37 900	92.4	94.3	0.990	0.992
	50	36 600	95.9	95.9	0.992	0.997
2a	0	19 700	37.0	80.7	0.967	0.959
	10	15 600	79.6	89.9	0.983	0.981
	50	14 100	87.9	91.9	0.986	0.985
2b	0	25 700	44.5			
	10	29 200	88.1	91.9	0.986	0.987
	50	24 800	92.4	93.1	0.988	0.990
2c	0	44 700	56.5	85.9	0.976	0.968
	10	41 100	92.0	93.7	0.989	0.991
	50	36 500	94.4	95.4	0.992	0.994

Table 2. Polymerization results   [a] *p*-Xylene insoluble.

K Shimozawa et al
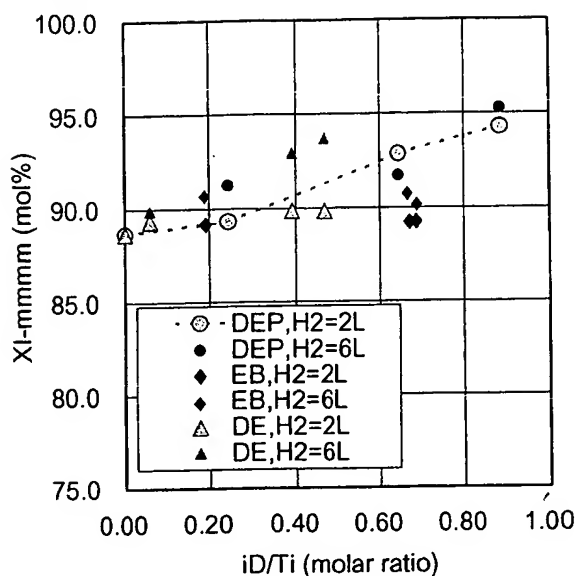
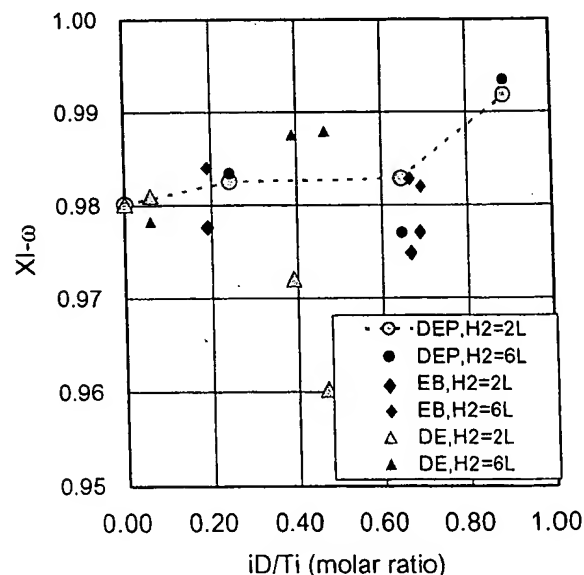
Figure 1. The relationship between XI-mmmm and iD/Ti.

the molar ratio of internal donor to Ti (iD/Ti) in the solid catalyst while Figs 2 and 3 show the relationship between α, ω and iD/Ti in the solid catalyst, respectively. Both cases included the results where polymerizations were conducted in and without the presence of external donor. Regardless of the presence of external donor, the value of α became larger with increase in iD/Ti. α also increased as Si/Ti in polymerization is raised. This means that α, the probability of the selection of d (l) monad in the asymmetric Bernoullian site, is attributed to both the amount of internal donor of catalyst component and the amount of external donor during polymerization relative to active centres (Ti).

The effects of internal donor and external donor on ω

ω shows an interesting profile for the range of this study where iD/Ti was varied using DEP as an internal donor. In the absence of external donor (Si/Ti = 0), ω becomes greater with increase of iD/Ti to reach its maximum at around iD/Ti = 0.5. However, it appears to drop gradually with further increase in iD/Ti. In contrast, in the case where external donor is incorporated, ω increases with the increase of iD/Ti, and sharply increase at a point where iD/Ti exceeds c 0.6.

These results may well imply a complementary function of the external donor on the formation of active isotactic polymerization centres for a specific region of iD/Ti in the catalyst component. We deduced the following hypothesis to account for such differences in the change of ω. In the region of iD/Ti < 0.6, the internal donor may be low enough in concentration to adsorb preferentially on strong acid sites. In this way, the internal donor resulted in an increase in asymmetric sites (ω) as well as an increase in the probability of selection of d (or l) monad (α). The presence of external donor favoured this trend probably by substituting the internal donor which was partly extracted by $Al(C_2H_5)_3$ during the course of polymerization. In the region of the higher internal donor concentration, some of asymmetric sites may lose their asymmetric configuration or just may become inactive by accepting coordination of excess internal donor molecules in their vicinity, which will come into effect to decrease ω. However, if the external donor is present, it may readily replace such weak internal donor after extraction by $Al(C_2H_5)_3$ and the active centres of the new kind are regenerated as asymmetry of the site is restored. This will lead to an increase in ω as well as an increase in the probability of selection of d (l) (α).

Figure 2. The relationship between XI-α and iD/Ti.

Figure 3. The relationship between XI-ω and iD/Ti.

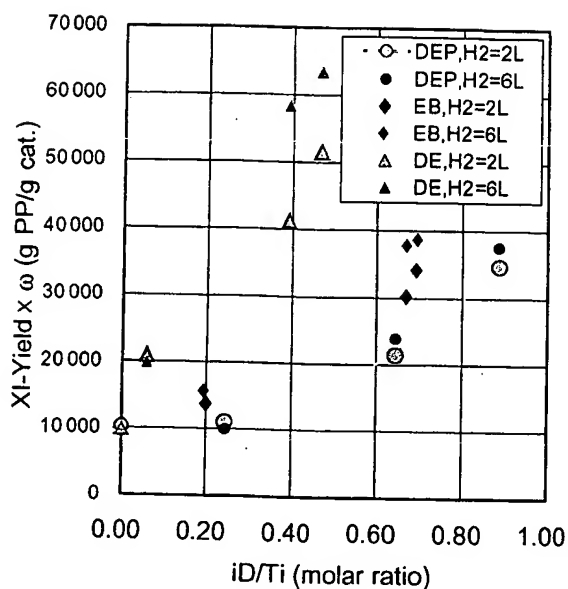Polym Int 51:530–533 (2002)

Figure 4. The relationship between α-site amount and iD/Ti.

The effects of the amount of hydrogen

The larger amount of hydrogen increased the mmmm for the diester-type catalysts, which is attributed mainly to the increase of α. The increase of mmmm was the largest for the diether-containing catalysts (catalyst 5a–5c) relative to the other two types of catalysts (mono-ester-containing type and di-ester-containing type). For the diether catalysts, ω as well as α were increased with a larger amount of hydrogen, which accelerates the increase of mmmm. As shown in Fig 4, the amount of alpha site (XI-Yield × ω) on the diether-containing catalysts was found to be increased by a larger amount of hydrogen, while almost no change was found for the other types of catalysts. This indicates that some of the sigma sites on the diether-containing catalysts worked alpha-sites-as with a larger amount of hydrogen, which increases ω as well as α and mmmm. While, for diester-type catalysts, mmmm was increased mainly by increasing of isotacticity of alpha-sites. EB-type catalysts indicated a similar behaviour to diester-type catalysts.

CONCLUSION

The two-site model was applied to obtain stochastic parameters for the $MgCl_2$/iD/$TiCl_4$ solid catalyst component used in combination with $Al(C_2H_5)_3$ and external donor for propylene polymerization. Both the concentration of internal donor of the catalyst component and that of external donor contributed to a higher probability in the selection of d (or l) monad in asymmetric site. With respect to the fraction for asymmetric site, the two-site model enabled us to conceive that the new kinds of active centres are generated in specific cases where external donor is believed to be replacing weaker internal donor during polymerization. An increase amount of hydrogen changed the manner of the steric regulation of a part of symmetric sites on the diether-containing catalysts, while it mainly increased the amount of asymmetric sites on di- and mono-ester-type catalysts.

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8 http://d-rep.sric.co.jp/twosite

Polypropylene and other Polyolefins

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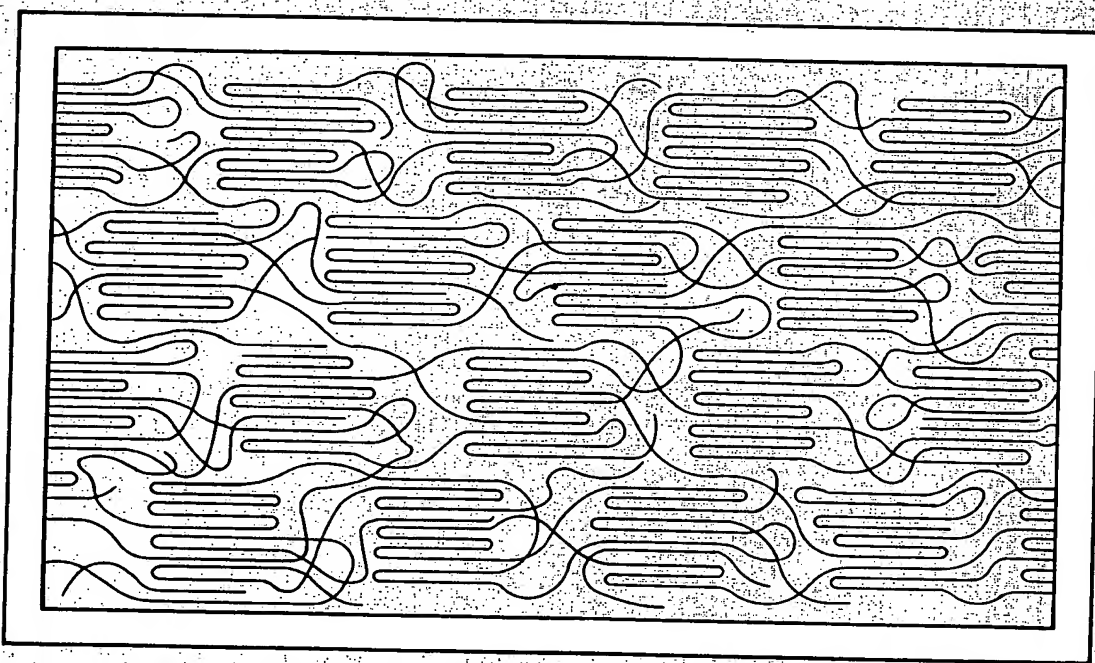
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Polypropylene and other Polyolefins

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The use of carborane anions in homogeneous Ziegler systems was also reported in a recent anonymous research disclosure[76] although the activity of these catalysts (up to 17,500 g polyethylene/g metal) is about an order of magnitude lower than that claimed by Turner[74]. In one example a catalyst, $Ti(C_2B_{10}H_{11})_4$, was used in combination with a methaluminoxane co-catalyst; in all other examples diethylaluminium chloride was applied.

1.5 CO-CATALYST CHEMISTRY

The previous sections describe the macro- and microstructure of the various Ziegler-Natta catalysts used commercially for the production of isotactic polypropylene. Although the term "catalyst" is the generally accepted nomenclature (and is used for convenience in this text) it is in fact a misnomer since the "catalyst" alone is not usually at all effective in catalyzing the polymerization; the "catalyst" must be activated by a co-catalyst comprising a metal alkyl from the groups I to III of the Periodic Table. Perhaps a more correct name for a $TiCl_3$ catalyst or supported catalyst would be the "pro-catalyst". This section describes the various types of co-catalysts used commercially and the interactions occurring between the co-catalyst and the pro-catalyst.

Although most alkyls of the group I to III metals are capable of generating active polymerization systems in combination with a suitable $TiCl_3$ catalyst, only aluminium alkyls are used in commercial operation. The uniqueness of aluminium alkyls can be attributed to both economic and technical factors. Aluminium alkyls such as triethyl aluminium have been commercially available on a large industrial scale since the 1950's, being manufactured via the relatively inexpensive, direct reaction between aluminium, hydrogen and the olefin. Most important however is the fact that by the appropriate choice of aluminium alkyl co-catalyst it is possible to generate highly stereoregular polyolefins, most other metal alkyls give significantly lower selectivity. Natta[77] was the first to report a correlation between polymer isotacticity and the choice of co-catalyst. Indeed Natta disclosed that polymer isotacticity, or in other words the stereoregulating ability of the resulting catalyst, is a function of the ionic radius of the metal in the metal alkyl chosen - the smallest ionic radius giving rise to the highest isotactic index. Natta's data is summarized in Table 1.3.

TABLE 1.3

Relationship between
the ionic radius of M

metal alkyl	ionic n
BeEt$_2$	3
AlEt$_3$	5
MgEt$_2$	6
ZnEt$_2$	7

* : polymerization of

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TABLE 1.3

Relationship between polypropylene isotacticity and
the ionic radius of M in MEtn

metal alkyl	ionic radius nm	isotactic index* %
$BeEt_2$	3.5	94 - 97
$AlEt_3$	5.1	80 - 90
$MgEt_2$	6.6	78 - 85
$ZnEt_2$	7.4	30 - 40

* : polymerization of propylene at 75°C using α-TiCl$_3$ catalyst

The acute toxicity of beryllium compounds makes the industrial application of $BeEt_2$ unacceptable. It should be noted that while there is obviously a distinct trend between ionic radius and isotactic index, care must be exercised when establishing such correlations since other factors such as the polymer molecular weight can greatly influence the polymer solubility in heptane, and hence its "apparent" isotactic index. Indeed both Boor[78] and Firsov and co-workers[79] reported that the crystallinity of zinc alkyl-derived polypropylene is significantly higher than suggested by Natta's findings but its low molecular weight results in a high solubility in heptane and a consequent low apparent isotactic index. The low molecular weight observed can be attributed to the efficient chain transfer capability of $ZnEt_2$ (see section 1.6).

A much more recent finding in the area of co-catalyst chemistry is that dimethylmetallocenes (e.g. Cp_2TiMe_2 and Cp_2ZrMe_2) act as excellent co-catalysts[80-82] with both $TiCl_3$ catalysts as well as supported systems[81]. In the case of a supported $TiCl_4$ on $MgCl_2$ catalyst (no electron donor) Soga[81] reported that using the series Cp_2MtMe_2 (Mt = V, Ti, Zr, Hf) as co-catalyst the vanadium and titanium systems gave high stereoselectivity (92 and 90% I.I. respectively) while the zirconium and hafnium analogues gave poor selectivity (61 and 69% I.I. respectively). Like Natta, Soga attributes the selectivity relationships to the ionic radii of the cocatalyst metals in the Cp_2MtMe_2 complexes (V, Ti, Zr, Hf being 7.2, 7.5, 8.5 and 8.6 nm respectively).

The following discussion will concentrate on the commercially significant aluminium alkyl co-catalysts. The differing nature of $TiCl_3$ catalysts and supported catalysts results in different types of co-catalysts being used; generally speaking dialkylaluminium

halides, frequently diethyl aluminium chloride (DEAC), are applied with TiCl$_3$ catalysts whereas supported catalysts require the application of trialkyl aluminiums, frequently triethylaluminium (TEA), in order to achieve optimum catalyst activity. In both cases "third components" (electron donors) are frequently employed in order to improve the performance of a given catalyst system.

1.5.1 TiCl$_3$ catalysts

Within the family of aluminium alkyls the substitution of one of the alkyl groups in triethyl aluminiums by a halide ion has a large effect on the stereoselectivity of propylene polymerization. Natta and co-workers[83] and Danusso[84] investigated this phenomenon concluding that when used with any of the purple TiCl$_3$ modifications it was the nature of the alkyl aluminium which determined the product isotacticity. Typical data is given in Table 1.4, where it can be seen that among the ethyl derivatives Et$_2$AlI (DEAI) affords the highest isotacticity, although the selectivity improvement is only achieved at the cost of a dramatic loss in polymerization

TABLE 1.4

Stereoregularities and molecular weight of the fractions insoluble in boiling heptane of polypropylenes obtained with δ-TiCl$_3$ in conjunction with different aluminium compounds as co-catalysts

Alkylalu-minium compound	Triad distribution			Molecular weights	
	mm %	mr %	rr %	M_n*10^{-5}	M_w*10^{-5}
AlEt$_3$	94	4	2	0.89	6.9
AlEt$_2$Cl	94	4	2	1.3	13.3
AlEt$_2$Br	≈98	>1	<1	1.5	16.9
AlEt$_2$I	≈98	>1	<1	-	-

activity. Indeed it is now generally accepted that there is a reciprocal relationship between isotacticity and activity. Commercial systems invariably comprise TiCl$_3$/DEAC since DEAC offers an acceptable level of both activity and selectivity; furthermore the application of iodide- or bromide- based systems would introduce additional process complications related to corrosion and product (colour) problems. It should be noted however that DEAI is used commercially as a co-catalyst component in the manufacture of

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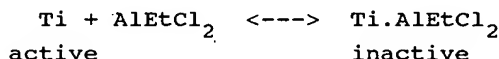ɔlymerization

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poly-1-butene (see chapter 11). The application of DEAI in polybutene is unavoidable due to the extreme difficulty of achieving acceptable isotacticity when using 1-butene as monomer.

In an elegant experimental study Keii[85] showed that a TiCl$_3$ catalyst could be endowed with the stereoselectivity of DEAI and the kinetics/rate of a DEAC system by initiating the polymerization with DEAI, washing and then continuing the polymerization using DEAC as co-catalyst.

In contrast to DEAC which is the co-catalyst of choice for TiCl$_3$ systems, ethyl aluminium dichloride (EADC) is a catalyst poison. Indeed even small amounts of EADC considerably reduce the rate of propylene polymerization using γ-TiCl$_3$/DEAC catalyst systems[17,86-88]. This rate lowering effect can best be explained in terms of a dynamic adsorption/desorption equilibrium between the surface TiCl$_3$ sites and EADC :

$$Ti + AlEtCl_2 \quad \longleftrightarrow \quad Ti.AlEtCl_2$$
$$\text{active} \qquad\qquad\qquad \text{inactive}$$

It is apparent that removal or complexation of EADC shifts this equilibrium to the left, effectively generating a larger number of active centres and therefore results in a higher polymerization rate.

The presence of EADC during the polymerization also affects product molecular weight substantially. This phenomenon is attributed to the same adsorption/desorption equilibria which can be used to explain deactivation. As illustrated in Fig. 1.25 EADC can become adsorbed to the active centre by one of two modes of complexation, and once adsorbed two modes of desorption can be envisaged. One of these desorption modes is effectively a chain transfer process (equilibria K_{12} and K_{22}; see also section 1.6). To a first approximation the molecular weight can be described as the ratio between the ratio of chain propagation (R_p) and chain termination (R_t) rates:

$$R_p/R_t = k_p[\text{propene}][Ti]/\{k_t[H_2][Ti] + (k_{12} + k_{22})K[Ti][EADC]\}$$

where $K = (k_1 + k_2)/(k_{11} + k_{12} + k_{21} + k_{22})$.

This relationship shows that product molecular weight is inversely proportional to the EADC concentration - therefore lowering the

54
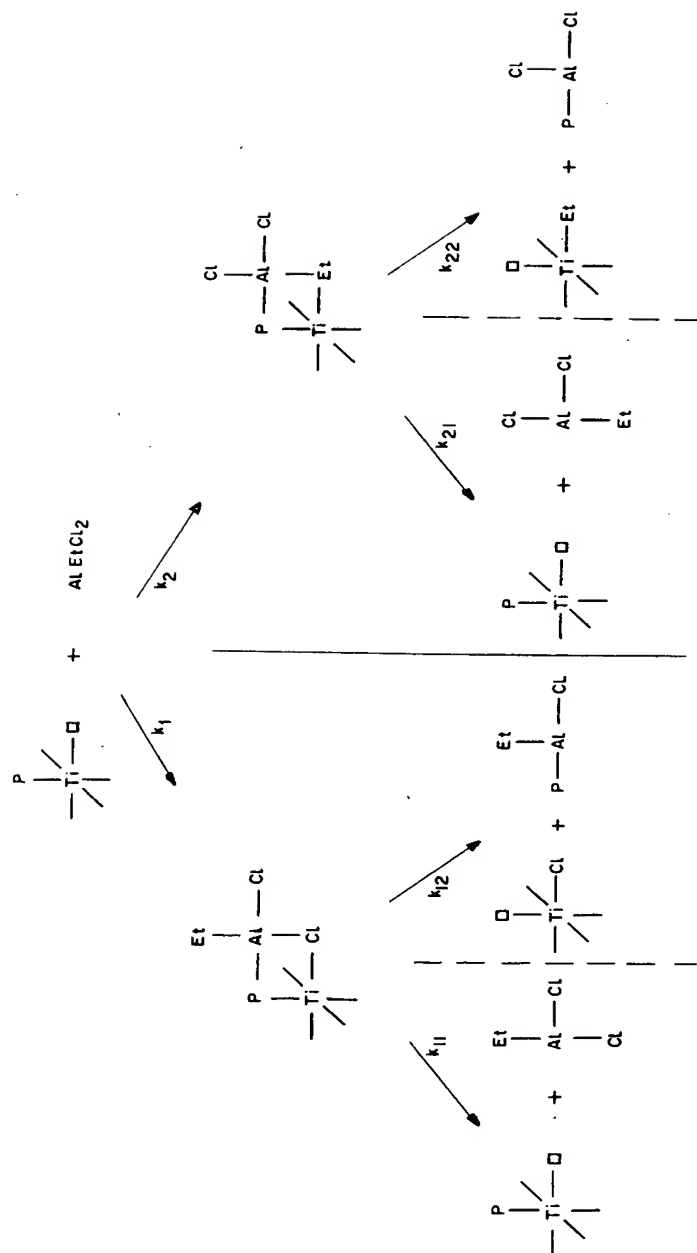
Fig. 1.25: Adsorption/desorption modes of AlEtCl$_2$ at active sites

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EADC concentration by extraction, complexation or simply reducing catalyst concentration results in higher product molecular weights.

In section 1.4 it was pointed out that the activity of $TiCl_3$ catalysts can be significantly increased by treatments (with ethers for example) which extract $AlCl_3$ from the solid and hence reduce the concentration of the catalyst poison EADC during the polymerization. Such catalyst activation procedures involve extra process steps in catalyst manufacture; furthermore the washing of fine catalysts would be exceedingly time-consuming, and hence commercially unattractive, because of the long settling times required after each washing step. For reasons of economy therefore, much research effort has been expended over the years aimed at finding Lewis base/co-catalyst combinations which can improve the activity and/or selectivity of a given $TiCl_3$ catalyst without involving extra catalyst manufacturing steps; the function of the Lewis base ("third component") in these systems is almost invariably to complex EADC, the most Lewis acid component of the co-catalyst. Boor (ref. 10, pages 213-243) argued that the role of Lewis bases is considerably more complex, but it is now generally accepted that for commercially important $TiCl_3$/DEAC systems it is complexation of the catalyst poison EADC which is the single most significant factor.

The effects of some simple Lewis bases on a typical (triethylaluminum-reduced) first generation $TiCl_3$ catalyst are shown in Table 1.5. The concentration of the Lewis base applied is of critical importance as is illustrated by the data given for dibutylether (DBE). Using different levels of DBE it was found that the polymerization activity could be improved by as much as 25% with no adverse effect on stereoselectivity (expressed in terms of yield stress) providing that the DBE/$TiCl_3$ ratio was no greater than 0.15; higher ratios resulted in a substantial loss of stereoselectivity. These results parallel the findings from studies on DBE washing of $TiCl_3$ catalysts (section 1.4.2) where a similar relationship was found between the DBE/$TiCl_3$ molar ratio employed and the final catalyst performance. Again it must be assumed that the fraction 0.15 corresponds to that portion of the $AlCl_3$ in the catalyst which exists as a separate phase, being readily soluble and hence reactive under polymerization conditions:

$$AlCl_3 + Et_2AlCl \longleftrightarrow 2\ EtAlCl_2$$
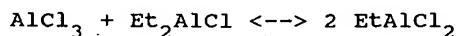
In the presence of a Lewis base such as DBE this equilibrium is driven back to the left as a result of DBE complexing the strongest Lewis acid in the system ($AlCl_3$).

TABLE 1.5

The effect of di-butyl ether and other Lewis bases on catalyst activity and yield stress (First generation TiCl3 catalyst).

Lewis base	base/$TiCl_3$, molar ratio	activity, gPP/g $TiCl_3$.h.bar	yield stress, MN/m^2	melt index, g/10 min
-	-	55	36.0	4.0
dibutyl ether	0.13	64	36.5	3.3
,,	0.15	71	37.0	2.5
,,	0.18	66	35.0	3.4
,,	0.33	68	32.5	1.8
,,	1.0	56	20.0	7.6
tetrahydrofuran	0.15	64	36.5	5.1
diisopropyl ether	0.15	62	36.5	4.0
water	0.15	58	37.0	4.3
triethyl amine	0.15	58	38.0	3.6
tetramethyl-methylenediamine	0.1	54	38.0	3.2
hexamethyl-phosphortriamide	0.05	55	39.0	3.2

Other ethers such as tetrahydrofuran and diisopropylether gave similar results. Nitrogen donors on the other hand were found to increase stereoselectivity without affecting catalyst activity; hexamethylphosphortriamide gave the best results in this respect.

A variation on the theme of "third components" involves the application of active hydrogen-containing species, such as alco-
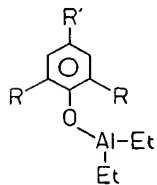
Fig. 1.26: Sterically-hindered phenoxy-substituted aluminium alkyl

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TABLE 1.6

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hols, which can react with aluminium alkyls to generate new, well-defined co-catalyst species. Particularly good results were obtained by applying sterically-hindered phenols[89]. Danusso[84] reported diethyl aluminium phenoxide (Fig. 1.26, R=R'=H) to be inactive as co-catalyst, the well-known[90] association of this species into dimers and trimers must be considered responsible for this lack of activity. Introducing severe steric hindrance into both ortho-positions (e.g. by reacting TEA with IONOL to afford the species shown in Fig. 1.26 (R=tert.-butyl, R'=methyl) suppresses self association leaving the active monomer species in solution. These sterically-hindered phenoxy co-catalysts were tested in combination with a second generation $TiCl_3$ catalyst prepared by reducing $TiCl_4$ with TEA in the presence of ether followed by heating in excess $TiCl_4$ at 110°C, to afford a dark purple $TiCl_3$ catalyst containing about 5% $AlCl_3$ (compared to first generation catalysts which contain typically 33% $AlCl_3$ – see section 1.4). Typical polymerization data are listed in Table 1.6 where in a standard run (DEAC co-catalyst) the catalyst showed good activity (141 gPP/g $TiCl_3$.bar.h) and reasonable, but not commercially acceptable, stereoselectivity (7.8 %m/m xylene solubles).

TABLE 1.6

Polymerization experiments with Ionol-modified co-catalysts

Ionol, mmol.	$AliBu_3$, mmol.	$AlEt_3$, mmol.	$AlEt_2Cl$, mmol.	$AlEtCl_2$, mmol.	activity gPP/g $TiCl_3$.bar.h	xylene solubles, %m/m
-	-	-	9	-	141	7.8
4	-	4	-	-	158	>20
4	-	4	-	4	178	2.3
4	-	-	8	-	144	1.8
4	4	-	-	-	300	>20
4	4	-	-	4	206	1.3

The new co-catalyst (the reaction product of equimolar amounts TEA and IONOL) was found to improve the polymerization activity somewhat but at the expense of stereoselectivity which decreased drastically (entry 2). Remarkably, mixing equimolar proportions of the species with EADC (catalyst poison!) led to a significant improvement (entry 3) in both activity (by about 30%) and stereoselectivity (2.3%m/m xylene solubles). Reacting IONOL with DEAC

(molar ratio 1:2) also gave excellent catalyst performance.

We ascribe the poor stereoselectivity of the TEA/IONOL co-catalyst to the inherent instability of the monomeric species[91] which can undergo a redistribution reaction liberating triethyl aluminium, which is known to result in poorly isotactic polymers :

$$2(RO)AlEt_2 \longleftrightarrow (RO)_2AlEt + AlEt_3$$
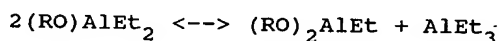
On the other hand we attribute the excellent performance of the EADC modified and DEAC analogues to the presence of chloride bridges which "stabilize" the sterically-hindered species preventing the above-described redistribution reaction (Fig. 1.27).

Fig. 1.27: Reaction of hindered phenol with DEAC

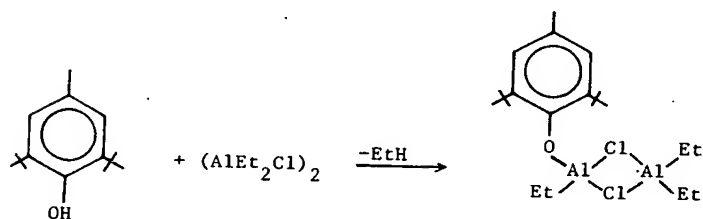An even better result was found when the degree of steric-hindrance was further increased by using triisobutylaluminium instead of TEA. As shown in Table 1.6 (entry 6) application of the IONOL/-triisobutylaluminium/EADC co-catalyst increased catalyst activity (compared to the standard DEAC run) by virtually 50% while at the same time demonstrating unprecedented stereoselectivity.

The outstanding activity achieved with these co-catalysts can be explained by considering that they selectively complex the
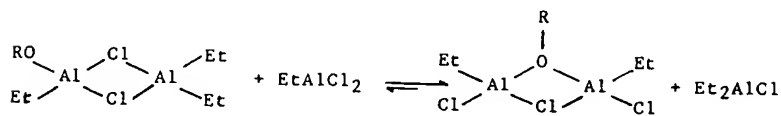
Fig. 1.28: Reaction of phenoxy-aluminium alkyl with EADC

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catalyst poison EADC as illustrated in Fig. 1.28. That these species are exceptionally efficient in this respect is due to the Lewis basicity of the phenoxy group combined with its severe steric hindrance which allow it to form strong complexes only with the very least sterically demanding Lewis acid in the system: EADC.

Interestingly these same sterically hindered phenoxy aluminium co-catalysts were found to double the activity of a β-TiCl$_3$ catalyst applied in "high-cis" isoprene rubber preparation[92]. Again the performance improvement must be attributed to efficient complexation of the EADC catalyst poison.

1.5.2 Supported catalysts

The co-catalyst of choice for supported catalysts are trialkyl aluminiums, the most commonly applied co-catalysts being triethyl- and triisobutyl aluminium. Other organometallic compounds such as DEAC or diethyl zinc result in very low polymerization rates.

Although TEA as co-catalyst leads to exceedingly high activities the stereoselectivity achieved is typically very poor (isotactic index 50-70%). Indeed the production of highly isotactic polypropylene requires the application of an electron-donor-modified co-catalyst. In the case of a typical MgCl$_2$/EB/TiCl$_4$ supported catalyst (section 1.4.3) the electron donors or "selectivity control agents" of choice are aromatic esters such as ethyl benzoate or para-ethyl anisate, higher concentrations of these esters, i.e. lower TEA/ester ratios, favouring higher stereoselectivity. Unlike simple Lewis bases such as the ethers or tertiary amines used with TiCl$_3$ catalysts, aromatic esters can undergo irreversible chemical reactions with trialkyl aluminiums under polymerization conditions. It can be learned from the literature[93,94] that the reactions are complex and that consecutive steps involving alkylation, reduction and elimination can lead to a multiplicity of products. The reactive nature of these mixtures makes the co-catalyst chemistry of supported catalysts substantially more complex than that of TiCl$_3$ systems.

After a study of the reactivity towards trialkyl aluminiums of a range of esters and ketones it was found that in the case of aromatic esters a TEA/ester molar ratio of >2:1 is required to give a reaction at typical polymerization temperatures (60-70°C). In the case of a commonly described selectivity control agent, para-ethyl anisate, the reaction was shown to be a clean, two-step alkylation reaction affording a new alkoxy aluminium dialkyl species as shown
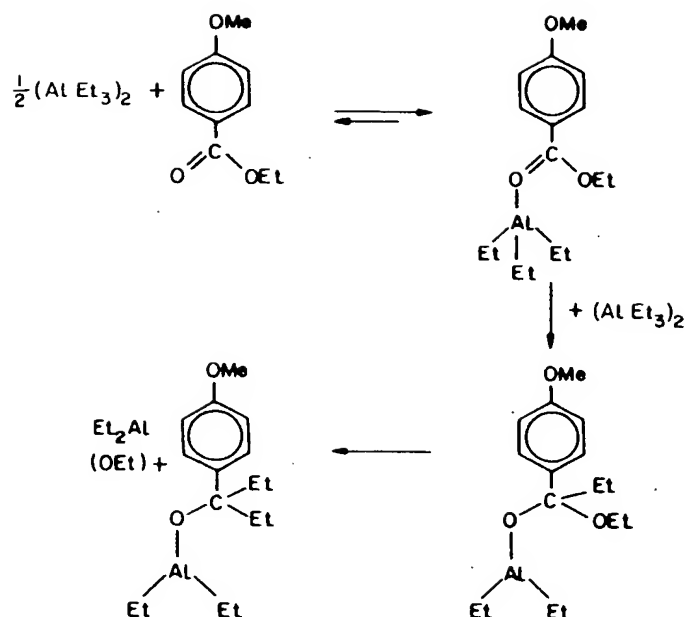
Fig. 1.29: The alkylation of ethyl anisate [from reference 158, copied with permission from Harwood Academic Publishers]

in Fig. 1.29. The reaction was studied under fairly concentrated conditions in perdeuterotoluene allowing the reaction to be monitored by ^{13}C-NMR methods, as illustrated in Fig. 1.30. At ambient temperature a simple adduct of TEA and the ester was formed, as witnessed by a yellow colouration of the solution and small shifts in the ^{13}C-NMR spectrum. If the molar ratio is held at 1:1 the reaction proceeds no further, even after extended heating at 60°C. However at a TEA/ester molar ratio of 3:1 (in polymerization runs with para ethyl anisate a molar ratio of 2.5 to 3.5 :1 is typically used) further reaction occurs, slowly at ambient temperatures, and rapidly at 60°C, to afford a colourless solution of the new alkoxy aluminium species (Fig. 1.29) resulting from double alkylation of the carbonyl function. In the course of these studies it was observed that the reactivity of aromatic esters towards TEA was strongly dependent not only on the molar ratio of the components and temperature, but also on the concentration and solvent used.

Langer and co-workers[95] studied the reaction between TEA and ethyl benzoate using proton NMR techniques, coming to similar
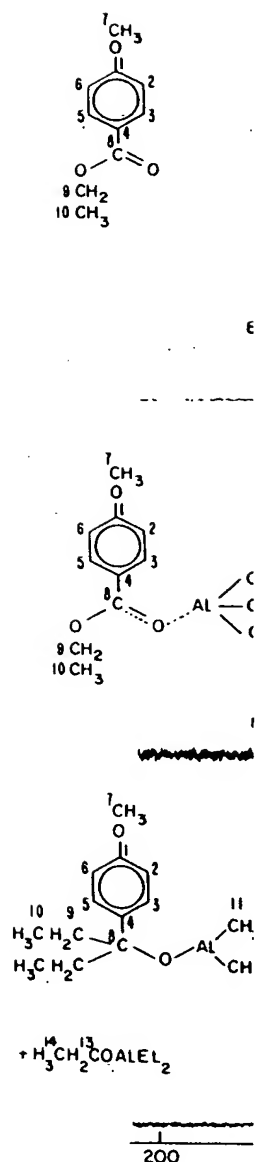
Fig. 1.30: ^{13}C-NMR s
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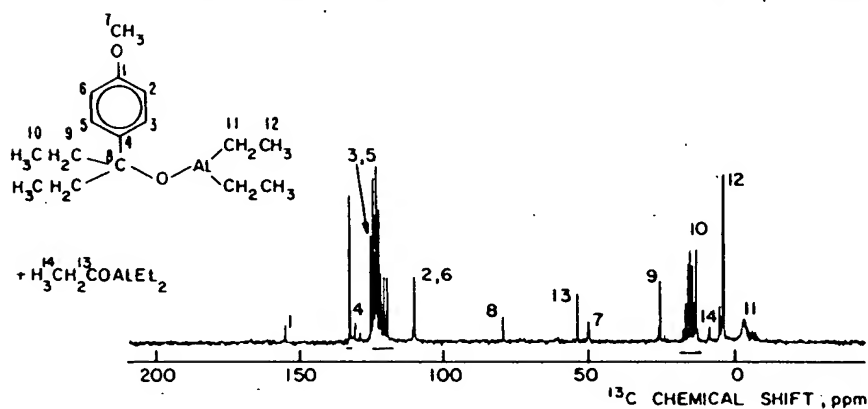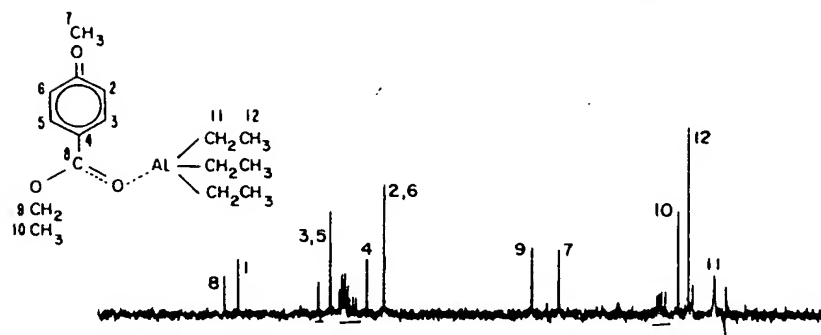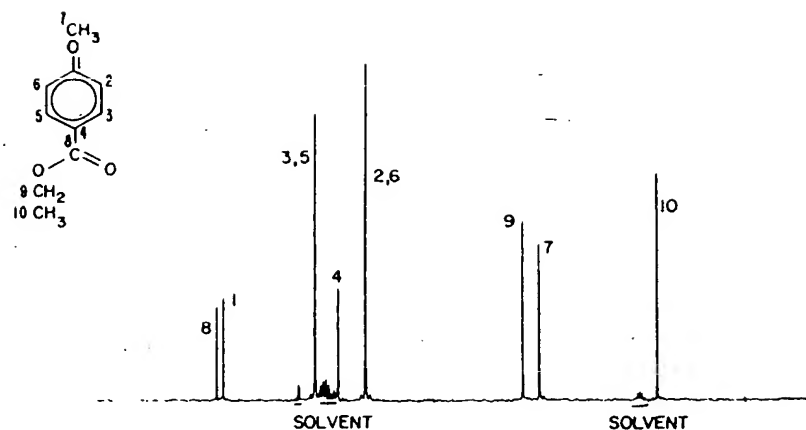
Fig. 1.30: ^{13}*C-NMR spectra of ethyl anisate and its reaction products with TEA [from reference 158, copied with permission from Harwood Academic Publishers]*

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conclusions regarding the reactions occurring. They reported no alkylation to occur at 25°C and 1:1 stoichiometry, at molar ratios >1 and <3 the reaction is initially rapid but than slows dramatically, while at a TEA/ester ratio of >3 the reaction proceeded to complete conversion (Fig. 1.31). The same authors furthermore discovered that the rate of alkylation could be greatly reduced by using sterically-hindered trialkyl aluminium compounds instead of
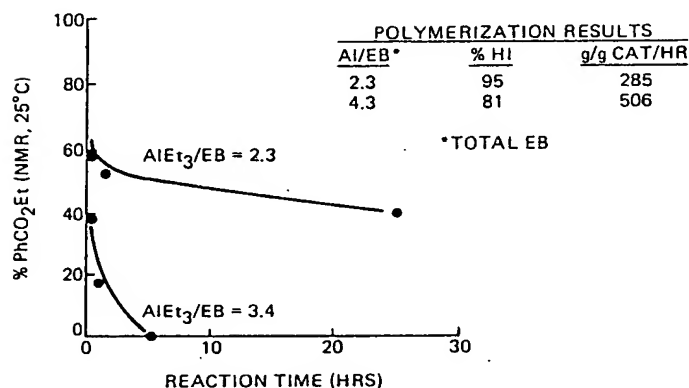
Fig. 1.31: Effect of $AlEt_3$/ethyl benzoate(EB) ratio on consumption of EB as a function of time (proton-NMR). Also shown are the polymerization results carried out at two $AlEt_3$/EB ratio's (%HI=%boiling heptane insolubles) [from reference 95, copied with permission from Plenum Press]

Fig. 1.32: Ethyl ber
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TEA, their results being illustrated in Fig. 1.32. Remarkably it was observed that during polymerization studies at low ethyl benzoate concentration (AlR_3 : EB molar ratio 4.3) which gives poor stereoselectivity using TEA as co-catalyst (82% isotactic index), much higher selectivity was observed when the sterically hindered trialkyl aluminiums were applied (Table 1.7). The fact that the increasing stereoselectivity parallels the decreasing ester alkylation rates led Langer et al to conclude that it is the ethyl benzoate itself which accounts for the high isotacticity attainable with these catalysts and not the alkoxy aluminium species which are formed during the alkylation process.

Another approach[95] to circumventing the ester alkylation reaction involved the use of sterically hindered esters, the rates of alkylation of which are known[96] to be substantially lower. In

TABLE 1.7
Effect of hindered

AlR_3	ra g/g c
$AlEt_3$	5(
$AliBu_3$	5:
sBu_2AlEt	5(
tBu_2AlEt	4(
sBu_3Al	4(

(1.0 mmol AlR_3, 0.2

They reported no
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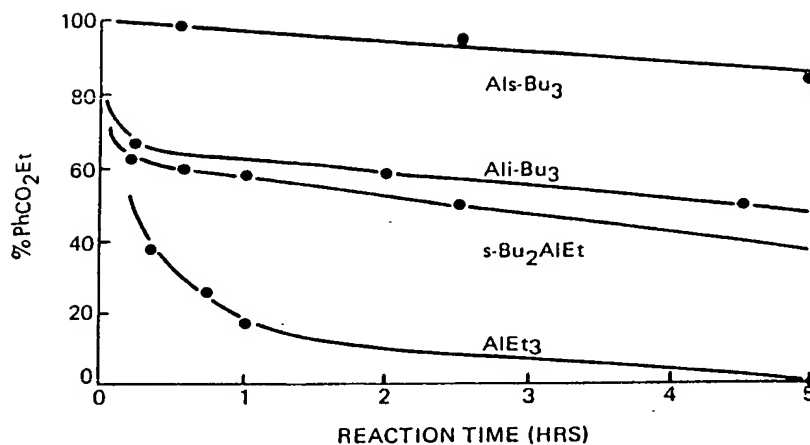
Fig. 1.32: Ethyl benzoate consumption as a function of time for several hindered AlR₃ compounds (proton-NMR) [from reference 95, copied with permission from Plenum Press]

nsumption of EB as a
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the series ethyl-, n-butyl-, iso-butyl- and tert.butyl benzoate the effectiveness of improving the isotactic index was found to decrease with increasing steric hindrance as shown in Table 1.8. On the basis of these findings the authors concluded that some sort of catalyst-ester interaction is required in order to achieve high

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TABLE 1.7

Effect of hindered AlR3's on catalyst performance (from ref. 95)

AlR₃	rate g/g cat.h	II,%m/m (heptane insolubles)	M_w*10^{-3}
AlEt₃	506	82	238
AliBu₃	520	88	315
sBu₂AlEt	501	89	307
tBu₂AlEt	489	90	313
sBu₃Al	461	92	357

(1.0 mmol AlR₃, 0.2 g catalyst)

isotacticity, and that this interaction is also disfavoured by increasing steric hindrance. A similar argument was used to explain the mediocre isotacticity achieved using 2,6-dimethyl substituted ethyl benzoate (Table 1.8); under NMR concentration conditions and at 25°C this ester was found to be alkylated very slowly indeed (22% in 22 hours).

TABLE 1.8

Hindered esters as third components (from ref. 95)

catalyst type	$AlEt_3$, mmol	ester, mmol	rate, g/g cat.h	II, %m/m	$M_w *10$
B1	0.4	0.12 $PhCO_2Et$	310	95	378
,,	,,	0.12 $PhCO_2n$-Bu	336	91	319
,,	,,	0.12 $PhCO_2i$-Bu	406	87	302
,,	,,	0.12 $PhCO_2t$-Bu	401	73	233
A1	1.0	0.2 $PhCO_2Et$	285	95	421
,,	,,	0.2 a)	378	89	303

a) 2,6-dimethyl-1-phenyl as a para-substituent on ethylbenzoate

On the basis of the foregoing we assume that the interaction between the catalyst and the ester, which accounts for stereoselectivity improvement, is again the ester alkylation reaction, but involving Ti-C bonds rather than Al-C bonds:

$$Ti-R + O=C \longrightarrow Ti-O-C-R$$
$$\text{deactivated site}$$

R is a growing polymer chain or alkyl group.
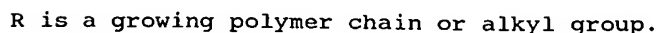
Indeed it is known that group IV (Ti, Zr) metal alkyls are even more reactive towards esters and ketones than are aluminium alkyls[97,98]. We suggest that the atactic sites are less hindered, or more exposed (Cossee model, see section 1.7) and hence more reactive towards the ester than are the isotactic sites: however this alkylation process also occurs, albeit slower, at the isotactic centres contributing significantly to catalyst deactivation. It would therefore appear that in choosing an aromatic ester as third component a careful balance in properties must be found:

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- if the ester is _too_ _unreactive_ towards alkylation (e.g. sterically hindered esters such as tertiary butyl benzoate) little or no improvement in isotactic index is observed (although less catalyst deactivation and a higher average polymerization rate is also seen).

- if the ester is _too_ _reactive_ towards alkylation (e.g. an aliphatic ester, or even ethyl benzoate) then it is either completely consumed by the TEA co-catalyst during premixing, resulting in no selectivity improvement, or it rapidly deactivates or poisons the catalyst by inserting into the Ti-C bonds.

It has been shown[93,94] for aromatic esters that the reactivity can be steered by suitable substitution of the aromatic nucleus; electron-donating substituents such as methyl and methoxy were shown to reduce reactivity, explaining why ethyl anisate and toluate are preferred to ethyl benzoate. On the other hand the introduction of too many electron-donating substituents, as in 2,4,6-trimethyl substituted EB for example, so greatly reduces the reactivity of the ester function that little or no effect on stereoselectivity is observed. Reviewing the more than three hundred patents describing stereospecific supported catalysts (those containing ethylbenzoate or analogues as "internal donor") for propylene polymerization we found that almost without exception the third component utilized could be defined as a para-substituted ester of benzoic acid, with H, CH_3, OCH_3 and OC_2H_5 as possible para substituents, whilst the ester is either methyl or ethyl.

The fact that aromatic esters undergo irreversible reactions with the trialkyl aluminium co-catalyst dictates that it is frequently not possible (or at least not advisable!) to mix these components more than a few minutes before the polymerization reaction is commenced.

Having discussed why most supported catalysts for propylene polymerization are used in combination with an aromatic ester third component, and the chemistry involved as a result, it is perhaps interesting to consider those systems which form exceptions in that esters are not applied to improve isotacticity. One series of exceptions takes the form of early patents[99,100] from Mitsui Petrochemical which described solid catalyst components containing ethyl benzoate as internal donor which were tested in polymeriza-

tions using TEA as co-catalyst but no external donor, and yet the selectivity achieved was in excess of 90% in many cases (for example 90.7% isotactic index in one case[100] with a polymer yield of 9.8 kg/g catalyst - 70°C, 3 h at 7 bar propylene pressure). This is probably explained by the fact that no molecular weight control by hydrogen was applied in these cases. Another system where no ester is applied as external donor is to be found in a Mitsubishi Petrochemical patent[101] where remarkably high isotacticity (97.6%) was reported in the absence of an external donor. In this case an apparently standard ball-milled $MgCl_2/EB/TiCl_4$ catalyst was treated with ICl_3 or iodine and washed prior to polymerization. It is possible in this case that an iodine (or iodide) ligand is incorporated into the active titanium centres resulting in the observed stereoselectivity improvement; in this case this work is obviously related to the work of Doi and Keii on iodine-modified $TiCl_3$ catalysts (see section 1.5.1).

Other remarkable exceptions include a series of patents of Denki[102,103] describing the use of sodium tetraethyl aluminate as co-catalyst, again in the absence of an external donor. A comparative example[102] reports TEA to give poor results (51.4% isotactic index) while the sodium salt ($NaAlEt_4$) yields high stereoselectivity (94.3% isotactic index) with the same solid catalyst component. This surprising result perhaps implies that the active centre is a cationic species:

$$-Ti-Cl + NaAlEt_4 \longrightarrow -Ti^+[AlEt_4^-] + NaCl$$
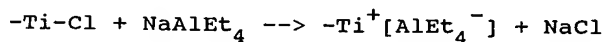
A precedent for this concept is to be found in early publications by Russian workers[72,73,104] who demonstrated the presence of cationic titanium species in the homogeneous $Cp_2TiCl_2/AlRCl_2$ system:

$$Cp_2TiRCl.AlRCl_2 \longleftrightarrow [Cp_2TiR]^+ + [AlRCl_3]^-$$
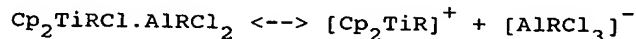
For further discussion on the possible role played by cationic species in Ziegler catalysis the reader is referred back to section 1.4.4.

Using $Cp_2Ti(CH_3)_2$ as sole co-catalyst with internal-donor free $TiCl_4/MgCl_2$ (ball-milled) pro-catalyst relatively high isotacticities are found, as reported by Soga et al[81,105]. The stereospe-

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TABLE 1.9
Sterically-hindered
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$Me_3SiCH_2AlEt_2$
$(neopentyl)_2AlEt$
$neopentylAlEt_2$
$(2-norbornyl)_2AliB$
$(s-Bu)_2AlEt$

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cificity can be improved from 90 to 97 % when the titanium content of the pro-catalyst is diminished fivefold, at the expense of activity[82]. Adding an external donor (EB) to such a catalytic system lowers the activity drastically.

It would be impossible to review this field of co-catalyst chemistry without referring to the elegant studies of Langer and co-workers at Exxon's laboratories involving the application of various types of sterically-hindered co-catalysts to typical ball-milled MgCl$_2$/EB/TiCl$_4$ catalysts. Some typical examples[106] are listed in Table 1.9. This remarkable effect on stereoselectivity is, in our opinion, best attributed to the monomeric nature of these co-catalyst species, formation of dimers (the predominant form in the case of TEA) being prevented by the sterically-deman-

TABLE 1.9

Sterically-hindered trialkylaluminium co-catalysts: effects on polymerization activity and selectivity* (from reference 106)

AlR$_3$	activity, g PP/g cat	selectivity, heptane insolubles, %m/m
AlEt$_3$	244	83.1
(Me$_3$SiCH$_2$)$_2$AlEt	182	90.8
Me$_3$SiCH$_2$AlEt$_2$	140	92.9
(neopentyl)$_2$AlEt	182	93.1
neopentylAlEt$_2$	227	91.9
(2-norbornyl)$_2$AliBu	247	91.8
(s-Bu)$_2$AlEt	357	93

*:supported catalyst prepared by ball-milling MgCl$_2$ with ethyl benzoate and treating with TiCl$_4$. Polymerization conditions: 1 bar, 65°C, 1 hour.

ding alkyl groups. Although not fully understood it would appear that the active centres generated between the surface titanium sites and the monomeric aluminium species possess a high stereospecificity (see also section 1.7). Unfortunately the real value of these systems must remain in some doubt since no data is presented

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under commercially representative conditions (high pressures, hydrogen for molecular weight control).

Although diethyl aluminium chloride itself is a very poor co-catalyst when used with supported catalysts there are reports in the patent literature[107,108] describing its beneficial effect when used in combination with a typical TEA and aromatic ester co-catalyst system.

As pointed out in section 1.7 we believe that the surface titanium centres in a supported catalyst are four-coordinate. In the case of a conventional $TiCl_3$ catalyst such a titanium centre would have the octahedral, "double vacancy" geometry illustrated in Fig. 1.33a since the titanium ion could be forced into an octahedral environment by the surrounding crystal lattice. However, it would be a misconception to assume the same site geometry for
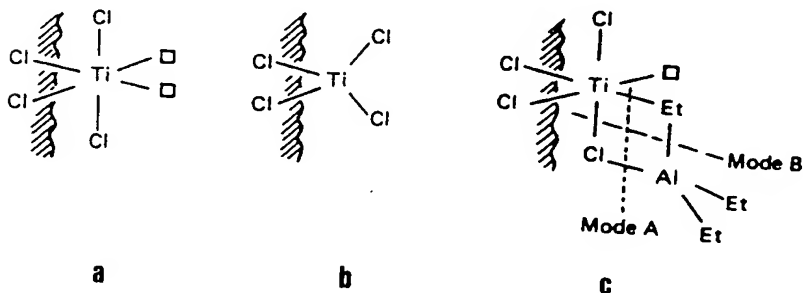

a   b   c

Fig. 1.33: Structure of surface site

supported catalysts, since in this case the $TiCl_4$ is simply adsorbed on to the support surface; as a result the four-coordinate titanium centres will assume the lower energy, tetrahedral geometry (Fig. 1.33b). This site will only assume octahedral geometry when complexed with TEA to give the active polymerization centre (Fig. 1.33c). The resulting active site can cleave in one of two ways (mode A and B in Fig. 1.33c) eliminating either TEA (mode A) or DEAC (mode B).

The whole process of titanium centre complexation and cleavage is represented in Fig. 1.34. The surface site is complexed by TEA (equilibrium i) to form the active site. Decomplexation of TEA
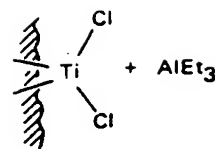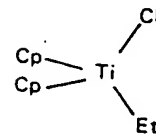

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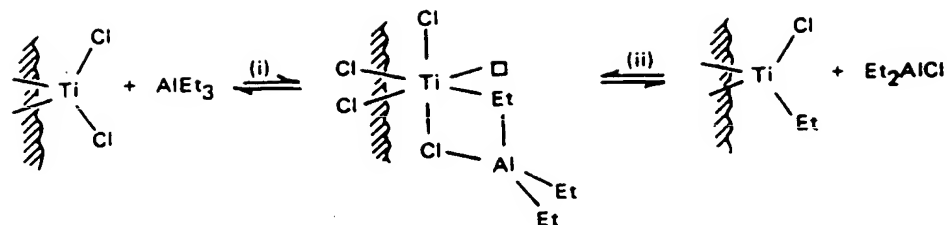Cp_2TiRCl plus RA:

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Fig. 1.35: Active ce

Fig. 1.34: Active centre formation

(i.e. cleavage via mode A) causes the titanium ion to revert to its original structure (n.b. during the polymerization process Et_2AlR, where R is the polymer chain, will be eliminated. In other words, equation i represents the chain transfer process). On the other hand cleavage via mode B (equilibrium ii) results in elimination of DEAC and causes the titanium ion to assume an alkylated, tetrahedral structure. While the titanium ions resulting from decomplexation are not deactivated, they are both "non-participating active centres" due to their tetrahedral, coordinatively-saturated geometry. These sites can only be converted into "participating active centres" by complexation with aluminium alkyls according to equilibria i and ii in Fig. 1.34.

A homogeneous model of the above concept is to be found in the well-known homogeneous ethylene polymerization catalyst system Cp_2TiRCl plus $RAlCl_2$[109]. In this case the pro-catalyst (Fig. 1.35a)
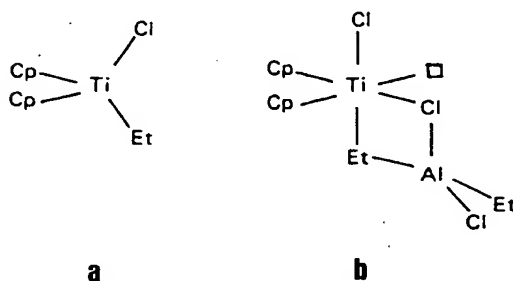
Fig. 1.35: Active centre formation in Cp_2TiCl_2

is totally inert towards olefins, until it is complexed by the co-catalyst which forces the titanium into an octahedral, coordinatively- unsaturated form (Fig. 1.35b). The careful reader will note the danger of drawing analogies however. In section 1.4.4 we reported the now convincing evidence that these homogeneous metallocene systems are in fact active by virtue of the formation of cationic species, in which the function of the alkylaluminium co-catalyst is to generate the stabilizing (and non-coordinating) anion. It should therefore be borne in mind that it is highly likely that cationic species are also the active centres in heterogeneous catalysts and that rather than representing titanium as a five-coordinate centre (e.g. Fig. 1.34) it would be more accurate to represent it as a three coordinate cation in the presence of an aluminium-based counterion.

Further examination of Fig. 1.34 reveals that the role of DEAC is to push equilibrium ii to the left converting non-participating sites into active centres, thus increasing the number of sites participating in the polymerization process. Of course the TEA concentration (or TEA/Ti molar ratio) has a similar effect of pushing equilibrium i to the right. Hence a co-catalyst comprising a TEA/DEAC mixture assures optimum catalyst performance by converting the maximum proportion of surface sites into active centres; the use of TEA alone results in a significant fraction of the sites being non-participating at any given time due to DEAC elimination.

Summing up, the co-catalyst of choice for application with most $MgCl_2$/aromatic ester/$TiCl_4$ supported catalysts comprises a trialkyl aluminium in combination with an aromatic ester such as para-ethyl anisate (PEA). In its most simple terms the method by which the external donor (PEA) improves stereoselectivity is by inserting preferentially into the Ti-C sigma bonds of atactic polymerization sites giving an inactive titanium alkoxide species. The fact that such alkoxide species can be realkylated by trialkyl aluminiums dictates that a controlled concentration of the external donor must be present throughout the polymerization.

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2.4 CHARACTERIZATION OF THE SOLUBLES

The most common method for characterizing polypropylene with respect to its stereoregularity is the determination of its "soluble" fraction in a specific solvent and at a specific condition. Two distinct procedures exist, one an extraction, the other a re-crystallization (see chapter 13 for details). Solvents used in the first procedure are often ethylether or heptane (at their boiling points), for the latter method xylene is frequently chosen. The material obtained in the extract or remaining in solution is referred to as the "ether solubles" or the "xylene solubles" of the particular sample of polypropylene. Solubles obtained by methods referred to above have been characterized in a number of ways, both in our own laboratory as elsewhere. The most important characteristics studied are tacticity, molecular weight distribution and crystallinity. In handling the material some data on its solubility have also been collected. Additionally an elaborate fractionation of xylene solubles will be described in this section, allowing firmer conclusions on the compositional distribution of this material. Finally some data on stereoblock polymers will be reviewed, this stereoblock polymer being a special kind of solubles.

2.4.1 Tacticity

The tacticity is usually measured by ^{13}C-NMR spectroscopy. An example of a ^{13}C-NMR spectrum of polypropylene solubles is given in Fig. 2.10. Generally speaking the fractions in mm, mr and rr are roughly equal, i.e. around 30%, with the overall diad figures of [m] just below 50%. There is no difference in the tacticity of the isopentane or the xylene solubles. Comparison with the expected spectrum of pure heterotactic material is instructive. Heterotactic material is defined as a random copolymer containing equal amounts of iso- and syndiotactic placements and the NMR spectrum would show a 1:2:1 ratio for the mm, mr and rr triads, with a further split within the triads in the same ratio. Clearly the solubles isolated are by no means heterotactic and a clear preference for both the iso- and syndiotactic triads is observed. Moreover, within these triads there is a preference for the pure iso- and pure syndiotactic pentads mmmm and rrrr. This means that the solubles are to be regarded as a copolymer of m and r placements with a very blocky nature.

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13.6.1 Polypropylene

In simple fractionation one is tempted to start with the solid polymer, however dissolution kinetics are very slow, see for example references 44 and 57. An example from our own experience is given in Table 13.4, but even with this relatively small polymer particle size the limiting value of polymer solubility is only reached in about 60 to 100 hours. This slow rate is due to the large molecules in polymers. The dissolution rate can be increased by employing a number of different measures:

- increase the temperature to lower the viscosity, increase diffusion, etc.

- minimize the dimensions of the specimen, at least in one direction,

- stir very intensively, the effect has already been mentioned above[54].

Even when using these improvements the result is still questionable, and the experimental procedure rather elaborate. A different situation arises when one starts from a solution of the polymer and allows one or more fractions to crystallize therefrom. By choosing

TABLE 13.5
Some methods used for measuring solubles in polypropylene

Used or originated by	Solvent	Tempe- rature	Time h	Polymer form	Approx. crys- tallinity of solubles by X-ray, %m/m
Natta[58,*]	n-heptane	reflux(100 °C)	24	powder or ground nibs	<20
Shell	diethyl- ether	reflux(35 °C)	2	powder	3
Shell	isopentane	room temp.	0.75	powder	1-5
FDA[59]	n-hexane	reflux(68 °C)	2	any form	(<10)**
FDA[59]	xylene	dissolve, crystallize at 25 °C	-	any form	2-10
FDA[59]	decalin	dissolve, crystallize at 25 °C	-	any form	(2-10)**

*: also ISO method R922

**: predicted

(FDA: the United States Food and Drug Administration)

the right conditions one can arrive very close to equilibrium.

Many different methods, some of which are summarized in table 13.5, are used by various institutes and industries to measure the amount of solubles present in polypropylene. Broadly speaking, the methods can be divided into two classes: one involves the washing of slurries and the other involves recrystallization from a (hot) solution. The values obtained using different methods vary widely, as the examples in table 13.6 show. The reason for this is that in all slurry washes the potentially soluble polymer has to migrate from the inside of the particles in which it was formed during the polymerization. Therefore factors such as the duration and the temperature of the washes, the base morphology of the powder or the sample shape markedly influence the results obtained. Consequently, great care has to be excercised when these solubles figures are used: they should always be quoted as the amount of solubles obtained by a certain specified method. The methods using recrystallization from a hot solution, such as the

TABLE 13.6
Examples of the results obtained by different solubles measurement methods

Method	Amount removed from		
	Sample A	Sample B	Sample C
	in %m/m		
isopentane, 25 °C, 45 min	1.0	2.2	-
isooctane, 25 °C, 45 min	0.68	2.0	0.11
n-hexane, 68 °C, 16 hours(a)	2.6	3.5	0.86
cyclohexane, 81 °C, 16 hours(a)	6.2	6.8	2.6
isooctane, 100 °C, 16 hours(a)	4.7	4.7	1.7
xylene, recrystallization	4.3	4.9	5.0

Sample A: made with low temperature reduced $TiCl_4$, particle size about 30 μ,

Sample B: made with $AlEt_2Cl$ reduced $TiCl_4$ as catalyst, particle size about 100 μ,

Sample C: made with Solvay catalyst, particle size about 200 μ.

(a): at reflux

xylene method (see table 13.5), are, however, not affected by these variables. In these methods, the separation of an isotactic fraction which is able to crystallize upon cooling and a fraction which stays in solution is obtained. More meaningful and consistent values are obtained in this way. This was already recognized early in the history of polypropylene, by scientists at Hoechst (ref 60)

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and others (ref 61). The Hoechst group later[62] gave additional evidence for their preference for this method.

The slurry wash methods can only be used successfully when no variations in morphology, particle size, etc. are expected. This would be the case in a manufacturing plant, although the results can only be used for plant control as they are not a true polymer characteristic.

In some of the studies reported in this book a recrystallization method will have been used. The method applied is either the standard xylene solubles method or a modified version. The xylene soluble method was originally described by Fuchs[60] and by the United States Food and Drug Administration[59]. In the xylene solubles method (abbreviated in this book by XS) one dissolves 2 grams of polymer in 200 ml of xylene (a mixture of isomers, with a boiling range of 137 to 143 °C) at around 120 °C, after dissolution this is cooled to 25 °C for 2 hours, and for analytical purposes a portion of the solution is filtered and an aliquot evaporated to dryness, the recovered weight being used in the calculation of the percentage soluble polymer. In a large number of cases one is interested not only in the soluble part of the polymer, but also in the recrystallizate. In that case one of course filters the total suspension and washes the solid with some fresh xylene.

In the modified method (called the hot xylene solubles, abbreviated to HOXS) the start of the test is the same, one cools to 25 °C for only 30 minutes after which the suspension is heated to 50 °C and kept at this temperature for another 30 minutes. Filtration is then effected through a thermostatted (50 °C) sintered glass funnel. By forcing this temperature profile on the mixture, equilibrium is very closely reached.

For a good understanding and interpretation of the data generated by this method, it is necessary to know the solubility of isotactic polypropylene under the final conditions of the test. Some data on this can be found in a publication of Natta's group[63], in which molecular weights of isotactic polypropylene soluble at the boiling points of various solvents are given. For instance in boiling ethylether a molecular weight of 2000 appears to be totally soluble (molecular weights based on osmotic pressure measurements), in pentane at 35 °C polypropylene of 3000 molecular weight is

soluble, in boiling n-hexane even 10,000. Some own data using GPC are given here. The solubility of two low molecular weight polypropylene samples in various solvents and at different temperatures is given in table 13.7. In the following table, 13.8, the characteris-

TABLE 13.7
Solubility of low molecular weight isotactic polypropylene

Base material: Two thermally degraded polymers from a common feedstock. The basestock was a non-extracted, melt index 3 polymer. The isotacticities([m]) measured by NMR were 91 % for the base material and 84 % for the degraded ones. Extraction method: 2 g of polymer was stirred with 100 ml solvent for two hours.

Sample	Solvent	Temperature, °C	Solubility, %m/m
Sample 1	isooctane	20	38
	do	70	70
M_v=1600	do	100	90
	isopentane	20	41
	tetrahydrofuran	20	42
	xylene	20	38
	cyclohexane	82 (reflux)	100
Sample 2	isooctane	20	20
	do	70	49
M_v=3000	isopentane	20	21
	tetrahydrofuran	20	21
	xylene	20	20
	cyclohexane	82 (reflux)	100

tics of some of the fractions obtained are given. At 20 °C isotactic polymer with a molecular weight of the order of 1400 is soluble in isooctane. Similar solubilities at 20 °C are observed in the other solvents except for cyclohexane, which is the best solvent for polypropylene. The solubility of isotactic polypropylene increases sharply when the temperature reaches values of higher than 70 °C (see table 13.7), so that for a method aiming at the determination of atactic polymer only, one should apply temperatures lower than 70 °C. For the described XS and HOXS methods this condition is fullfilled, which is not the case in the very frequently applied boiling heptane solubles method, operating at 100 °C.

Another illustrative set of data on the effect of extraction temperature on both the efficiency of atactic polypropylene removal from powder and on the level of co-extracted isotactic polypropyle-

TABLE 13.8
Characterization o

sample			
SAMPLE 1			
total			
isooctane soluble at 20 °C			
isooctane insoluble at 20 °C			
isooctane soluble at 70 °C			
isooctane insoluble at 70 °C			
SAMPLE 2			
total			
isooctane soluble at 20 °C			
isooctane insoluble at 20 °C			
isooctane soluble at 70 °C			

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At 20 °C isotac-
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C are observed in
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HOXS methods this
in the very fre-
operating at 100

ct of extraction
propylene removal
ctic polypropyle-

TABLE 13.8
Characterization of soluble low molecular weight isotactic polypropylene

sample	Crystal-linity, %m/m	DSC data Melting temperatures T_{ml}, °C	Crystal-lization temp. T_x °C	GPC data M_n	M_w	Q	R
SAMPLE 1							
total	31	128,161	82	1090	1420	1.30	1.42
isooctane soluble at 20 °C	27	31,46,69,81,88	-	1160	1390	1.20	1.27
isooctane insoluble at 20 °C	47	131	100	-	-	-	-
isooctane soluble at 70 °C	23	117	73	1280	1580	1.23	1.29
isooctane insoluble at 70 °C	21	135,156	101	1570	1960	1.25	1.30
SAMPLE 2							
total	35	138	91	-	-	-	-
isooctane soluble at 20 °C	22.5	10,30,43,68,81,87	-	980	1390	1.41	2.0
isooctane insoluble at 20 °C	45	141	105	-	-	-	-
isooctane soluble at 70 °C	-	-	-	1250	1780	1.43	1.62

ne is given in Table 13.9, where data are given of extractions at increasing temperature. The resulting extracts were re-extracted with isopentane at room temperature to separate them as far as possible into an isotactic and an atactic fraction. In Fig. 13.24 the molecular weight distributions of the latter are given. Clearly a fairly high temperature is required to extract a fair fraction of the atactic polymer present from the solid polymer, and at these high temperatures up to 50 % of the extract is isotactic. The parameters of the molecular weight distributions of the non-isopentane soluble part are given in table 13.10. Again increasing molecular weights with increasing temperature are noted, the absolute values are certainly lower than expected on the basis of Natta's work. There is an influence of the base polymer, which has been dealt with in chapter 2.

The efficiency of the XS method has been tested by a large number of re-extractions on residues from the first extraction. The amount in the second extraction is found to be 2 to 7 % of the

TABLE 13.9
Extractions of polypropylene at different temperatures
Base powder made with low temperature reduced $TiCl_4$, melt index 3.6, xylene solubles 4.3 %m/m (XS_0)

Sol-vent	Temp, °C	Amount remo-ved, %m/m	Xylene solu-bles of residue, %m/m	Fraction of XS_0 removed	Solubi-lity of extract in iC_5, %m/m	Crys-talli-nity, %m/m	Melting point, °C	M_n	Q	R
iC8	25	0.68	3.5	0.19	100	1	51,81	2100	9.5	15
nC7	25	0.99	3.5	0.19	100	0.2	55	-	-	-
iC5	25	0.99	3.3	0.23	100	2	30,52	2100	7.4	11
CyC6	25	1.1	3.4	0.21	n.d.	2	49	-	-	-
iC8	50	1.3	3.0	0.30	n.d.	3	37,53,77	2600	5.7	8.2
CyC6	50	2.0	2.5	0.42	n.d.	5	48,70	2800	7.0	9.1
CHCl3	62*	2.8	2.2	0.49	81	-	-	4200	6.3	20
nC6	68*	2.6	2.1	0.51	91	6	50,70,105	3200	5.5	6.9
iC8	75	2.1	2.4	0.44	96	7	50,96,148	3200	5.4	6.7
nC7	75	2.1	2.3	0.47	-	-	-	-	-	-
CC14	77*	3.9	1.5	0.65	58	-	-	4300	5.7	8.2
CyC6	82*	6.2	1.2	0.72	51	27	132	3200	7.0	4.8
nC7	98*	5.1	1.3	0.70	56	21	130	3800	5.1	4.0
iC8	99*	4.7	1.2	0.72	60	-	-	3400	5.2	4.2

*: reflux

GPC data of xylene solubles of original sample: $\bar{M}_n$:4600, Q=11, R=8.

TABLE 13.10
Molecular weight distribution parameters of isopentane insoluble parts of extracts removed at higher temperature

Solvent, wash conditions	M_n	Q	R	Peak mol wt
n-hexane, 68 °C	3800	20	17	2700
cyclohexane, 82 °C	3100	4	20	6140
isooctane, 99 °C	2900	9	19	4530
n-heptane, 98 °C	3000	5	18	5220

first value. The second extract is of higher crystallinity and shows a low molecular weight tail in its molecular weight distribution. A relative larger fraction of low MW isotactic polypropylene is thus present in this second extract.

A comparison of the amount of solubles obtained by both the XS

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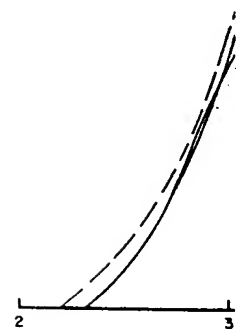SOLUBLE IN ISOPENTAN

Fig. 13.24: Molecul
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	Q	R
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	-	-
	7.4	11
	-	-
	5.7	8.2
	7.0	9.1
	6.3	20
	5.5	6.9
	5.4	6.7
	-	-
	5.7	8.2
	7.0	4.8
	5.1	4.0
	5.2	4.2

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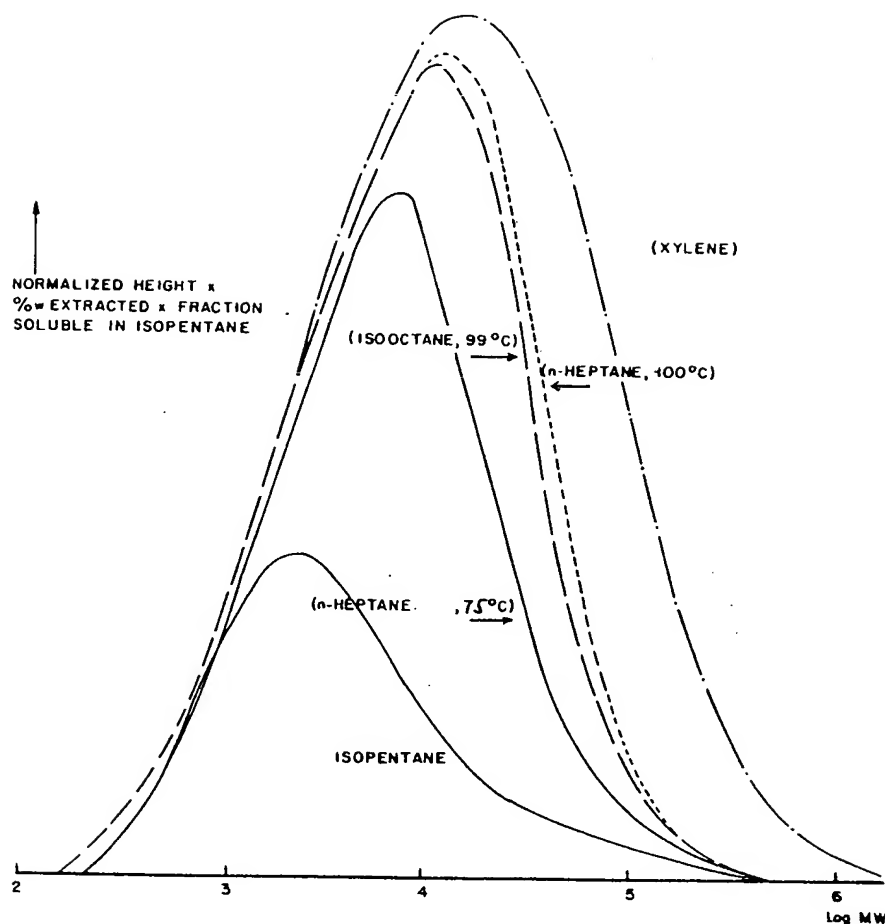>luble parts of

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Fig. 13.24: Molecular weight distributions of the isopentane soluble fractions obtained from extracts made at higher temperatures

and HOXS methods is given in table 13.11. As expected the HOXS value is greater but not by much, averaging about 1 to 1.5 % absolute in a vast range range of base polymer molecular weights. This also illustrates that the isotactic polypropylene solubility under the conditions of this test is low.

Kakugo et al describe[64] another very interesting fractionation method leading to four different fractions. This probably makes it a time consuming method, but considerable information is obtained.

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TABLE 13.11
Comparison of XS and HOXS on polypropylene homopolymer

Base polymer		Xylene solubles %m/m (XS)	Hot xylene solubles %m/m (HOXS)	Diffe-rence
LVN dl/g	Melt Index g/10min			
2.87	2.2	4.3	5.0	0.7
2.32	6.5	4.8	5.9	1.1
2.01	14	5.5	6.5	1.0
1.71	30	7.0	7.5	0.5
1.46	65	8.0	8.8	0.8
1.29	120	9.6	10.3	0.7
1.21	160	6.6	8.4	1.8
1.12	230	7.6	8.8	1.2

They start with a xylene recrystallization, and extend this proce-
dure with two subsequent boiling solvent fractionations with hexane
and heptane respectively, i.e. at about 70 and 100 °C. In this way
they remove selectively the so-called stereoblock polymer, the
quantities of which differ for different catalysts and polymeriza-
tion conditions (as also shown by a slightly different method in
chapter 2.4.6). It is claimed that the residue arrived at in this
method is of a constant, very high tacticity of 97% mm.

13.6.2 Polyethylene

Showing no tacticity, simple "solubles" tests for that purpose
are of course absent. However one frequently measures the low
molecular weight tail of the molecular weight distribution (the
so-called "wax") by a simple extraction. For instance extracting
PE-films with n-hexane for 2 hours at 50 °C is a much quoted
version of this test.

13.6.3 Poly(1-butene)

For isotactic poly(1-butene) also, fractionation or simple
extraction is the frequently-used tool to judge its stereoregula-
rity. Poly(1-butene) is more readily soluble in hydrocarbon sol-
vents compared to both polyethylene and polypropylene. For instance
the dissolution temperature in toluene is 39 °C and in n-heptane 35
°C. This means that a slurry polymerization can only be performed
at low temperatures of under about 40 °C in relatively poor sol-
vents such as the monomer itself.

The usual method for measuring the "atactic" level is extrac-

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